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EP05/2204



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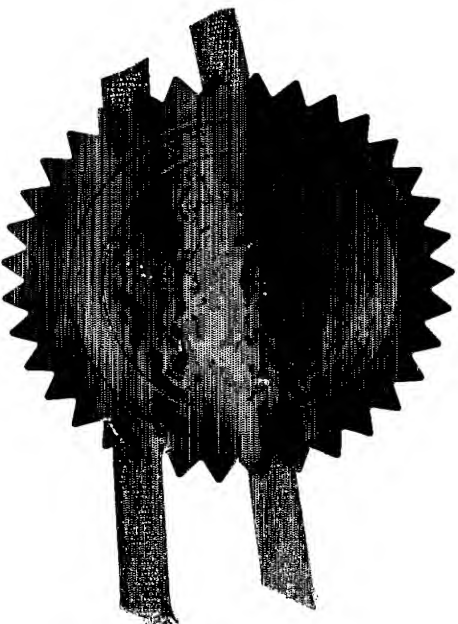
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Signed

H. Behen

Dated 4 January 2005

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GB0404801.3

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SYNGENTA PARTICIPATIONS AG
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The Patent Office

Cardiff Road
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South Wales
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1. Your reference

PI-70411P1

2. Patent application number

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0404801.3

- 3 MAR 2004

3. Full name, address and postcode of the or of each applicant (underline all surnames)

SYNGENTA PARTICIPATIONS AG
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Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

1524 93 (1977 ACT) APPLICATION FILED

14/10/04

4. Title of the invention

BICYCLIC DERIVATIVES

5. Name of your agent (if you have one)

Michael James RICKS

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Syngenta Limited
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Patents ADP number (if you know it)

01282433003

8029563001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

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Date of filing
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11.

I/We request the grant of a patent on the basis of this application.

SYNGENTA PARTICIPATIONS AG
Signature

Date 03/02/04

Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

J M BIDDLE

+44 (0) 1344 413672

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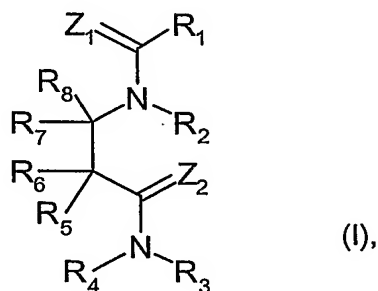
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Bicyclic derivatives

The invention relates (1) to compounds of the formula



in which

Z_1 is an oxygen atom; or a sulfur atom;

Z_2 is an oxygen atom; or a sulfur atom;

R_1 is an aryl or heteroaryl group, which is unsubstituted or substituted;

R_2 is hydrogen; or an organic substituent;

R_3 is hydrogen; or an organic substituent;

R_4 is hydrogen; or an organic substituent;

or R_3 and R_4 , taken together, form, together with the nitrogen atom, to which they are attached, a ring, which is unsubstituted or substituted;

R_5 is hydrogen; or an unsubstituted or substituted alkyl group; or forms, taken together with R_6 or with a monovalent substituent attached to that atom of R_6 , via which atom R_6 is directly connected with the carbon atom, shown in the formula I, which carries R_5 , one additional bond;

R_6 and R_7 , taken together, form, together with the two carbon atoms, shown in the formula I, to which atoms they are attached, a bicyclic ring system, which ring system is carbocyclic or heterocyclic, which ring system is substituted, in the manner shown in the formula I, by the four substituents $-N(R_2)-C(=Z_1)-R_1$, $-C(=Z_2)-N(R_3)-R_4$, R_5 and R_8 , and which ring system is optionally further substituted;

and R_8 is hydrogen; or an unsubstituted or substituted alkyl group; or forms, taken together with R_5 or with a monovalent substituent attached to that atom of R_7 , via which atom R_7 is directly connected with the carbon atom, shown in the formula I, which carries R_8 , one additional bond,

in free form or in salt form, where appropriate to tautomers, in free form or in salt form, of these compounds, to a process for the preparation and to the use of these compounds and

tautomers, to pesticidal compositions whose active ingredient is selected from amongst these compounds and tautomers, in each case in free form or in agrochemically utilizable salt form, to a process for the preparation and to the use of these compositions, to plant propagation material treated with these compositions, to a method of controlling pests with these active ingredients and compositions, to intermediates, in free form or in salt form, for the preparation of these compounds, where appropriate to tautomers, in free form or in salt form, of these intermediates, and to a process for the preparation and to the use of these intermediates.

Certain bicyclic derivatives have been proposed in the literature as arthropodacidally active ingredients in pesticides. However, the biological properties of these known compounds are not entirely satisfactory in the field of pest control, which is why there is a need to provide other compounds which have pesticidal properties, in particular for controlling insects and representatives of the order Acarina, this object being achieved according to the invention by providing the present compounds I.

In some cases, the compounds I can exist as tautomers. For example, if in the formula I the substituent $-N(R_2)-C(=Z_1)-R_1$ is $-N(R_2)-C(=O)-R_1$ and R_2 is hydrogen, corresponding compounds I, i. e. those in which $-N(R_2)-C(=Z_1)-R_1$ is $-N(H)-C(=O)-R_1$, can be in equilibrium with the respective tautomers, in which the respective substituent has the tautomeric structure $-N=C(OH)-R_1$. Accordingly, the compounds I hereinabove and hereinbelow are to be understood as including such tautomers, where appropriate, even though the latter are not mentioned specifically in each individual case.

Compounds I which have at least one basic centre can form, for example, acid addition salts, for example with strong inorganic acids such as mineral acids, for example perchloric acid, sulfuric acid, nitric acid, nitroic acid, a phosphorus acid or a hydrohalic acid, with strong organic carboxylic acids, such as C_1 - C_4 alkanecarboxylic acids which are unsubstituted or substituted, for example by halogen, for example acetic acid, such as saturated or unsaturated dicarboxylic acids, for example oxalic acid, malonic acid, succinic acid, maleic acid, fumaric acid or phthalic acid, such as hydroxycarboxylic acids, for example ascorbic acid, lactic acid, malic acid, tartaric acid or citric acid, or such as benzoic acid, or with organic sulfonic acids, such as C_1 - C_4 alkane- or arylsulfonic acids which are unsubstituted or substituted, for example by halogen, for example methane- or p-toluenesulfonic acid. Com-

pounds I which have at least one acidic group can form, for example, salts with bases, for example mineral salts such as alkali metal or alkaline earth metal salts, for example sodium, potassium or magnesium salts, or salts with ammonia or an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower-alkylamine, for example ethyl-, diethyl-, triethyl- or dimethylpropylamine, or a mono-, di- or trihydroxy-lower-alkylamine, for example mono-, di- or triethanolamine. Where appropriate, the corresponding internal salts can furthermore be formed. Preferred within the scope of the invention are agrochemically advantageous salts; however, the invention also encompasses salts which have disadvantage for agrochemical use, for example salts which are toxic to bees or fish, and which are employed, for example, for the isolation or purification of free compounds I or agrochemically utilizable salts thereof. Owing to the close relationship between the compounds I in free form and in the form of their salts, for the purposes of the invention the free compounds I or their salts hereinabove and hereinbelow are respectively to be understood as including, where appropriate, the corresponding salts or the free compounds I. The same applies analogously to tautomers of compounds I and salts thereof. In general, the free form is preferred in each case.

Preferably the invention relates (2) to a compound according to (1) of the formula I, in which

Z₁ is an oxygen atom; or a sulfur atom;

Z₂ is an oxygen atom; or a sulfur atom;

R₁ is a phenyl or naphthyl group, which is substituted independently by 1 or 2 substituents R_a and optionally further substituted independently by 1 to 3 substituents R_b;

R_a is cyano; nitro; halogen; C₁-C₆alkyl; halo-C₁-C₆alkyl; C₁-C₆alkoxy-C₁-C₆alkyl; C₂-C₆alkenyl; halo-C₂-C₆alkenyl; C₂-C₆alkynyl; halo-C₂-C₆alkynyl; C₃-C₆cycloalkyl; halo-C₃-C₆cycloalkyl; hydroxy; C₁-C₆alkoxy; halo-C₁-C₆alkoxy; C₃-C₆cycloalkoxy; mercapto; C₁-C₆alkylthio; halo-C₁-C₆alkylthio; C₁-C₆alkylsulfinyl; halo-C₁-C₆alkylsulfinyl; C₁-C₆alkylsulfonyl; halo-C₁-C₆alkylsulfonyl; amino; C₁-C₆alkylamino; halo-C₁-C₆alkylamino; di-C₁-C₆alkylamino, in which the two alkyl groups are the same or different or, taken together, form, together with the nitrogen atom, to which they are attached, a ring containing 1 ring nitrogen atom and 2 to 12 ring carbon atoms and optionally 1 further ring hetero atom, which then replaces 1 ring carbon atom and is selected from the group, consisting of an oxygen, a sulfur and a nitrogen atom, which ring is unsubstituted or substituted independently by 1 to 4 substituents, selected from the group, consisting of cyano, nitro, halogen, C₁-C₄alkyl and C₁-C₄alkoxy; di-(halo-C₁-C₆alkyl)-amino, in which the two haloalkyl groups are the same or different; C₃-

C₆cycloalkylamino; N-(C₁-C₆alkyl)-N-(C₃-C₆cycloalkyl)-amino; carboxy; C₁-C₆alkoxycarbonyl; halo-C₁-C₆alkoxycarbonyl; aminocarbonyl; C₁-C₆alkylaminocarbonyl; halo-C₁-C₆alkylaminocarbonyl; di-C₁-C₆alkylaminocarbonyl, in which the two alkyl groups are the same or different or, taken together, form, together with the nitrogen atom, to which they are attached, a ring containing 1 ring nitrogen atom and 2 to 12 ring carbon atoms and optionally 1 further ring hetero atom, which then replaces 1 ring carbon atom and is selected from the group, consisting of an oxygen, a sulfur and a nitrogen atom, which ring is unsubstituted or substituted independently by 1 to 4 substituents, selected from the group, consisting of cyano, nitro, halogen, C₁-C₄alkyl and C₁-C₄alkoxy; di-(halo-C₁-C₆alkyl)-aminocarbonyl, in which the two haloalkyl groups are the same or different; C₁-C₆alkylcarbonyl; halo-C₁-C₆alkylcarbonyl; or tri-C₁-C₆alkylsilyl, in which the three alkyl groups are the same or different;

or 2 substituents R_a, which are attached to adjacent carbon atoms, taken together, are -(CH₂)₃; -(CH₂)₄; -(CH₂)₅; -(CH=CH)₂; -OCH₂O-; -O-(CH₂)₂O-; -OCF₂O-; -(CF₂)₂O-; -O-(CF₂)₂; or -O-(CF₂)₂O-;

R_b is halogen; C₁-C₆alkyl; C₂-C₆alkenyl; C₂-C₆alkynyl; C₃-C₆cycloalkyl; C₁-C₆alkoxy; C₁-C₆alkoxycarbonyl; or a phenyl, benzyl, phenoxy or monocyclic or bicyclic heteroaryl group, which group is unsubstituted or substituted independently by 1 to 4 substituents, selected from the group, consisting of the substituents R_a;

or R₁ is a monocyclic or bicyclic heteroaryl group, which is unsubstituted or substituted independently by 1 to 4 substituents R_c;

R_c is a substituent R_a; or a phenyl, benzyl, benzoyl, phenoxy or monocyclic or bicyclic heteroaryl group, which group is unsubstituted or substituted independently by 1 to 4 substituents, selected from the group, consisting of the substituents R_a;

R₂ is hydrogen; a C₁-C₆alkyl, C₂-C₆alkenyl, C₂-C₆alkynyl or C₃-C₆cycloalkyl group, which group is unsubstituted or substituted independently by one or more substituents, selected from the group, consisting of the substituents R_a; a group C(=O)R_d; or a group C(=S)R_d;

R_d is a substituent R₁; C₁-C₆alkyl; halo-C₁-C₆alkyl; C₁-C₆alkoxy-C₁-C₆alkyl; a group CH₂R₁; a group CH₂OR₁; a group CH₂SR₁; a group CH₂NHR₁, which group is optionally further substituted at the nitrogen atom by C₁-C₆alkyl or halo-C₁-C₆alkyl; C₂-C₆alkenyl; halo-C₂-C₆alkenyl; C₂-C₆alkynyl; halo-C₂-C₆alkynyl; C₃-C₆cycloalkyl; halo-C₃-C₆cycloalkyl; C₁-C₆alkoxy; halo-C₁-C₆alkoxy; C₃-C₆cycloalkoxy; a group OR₁; C₁-C₆alkylthio; halo-C₁-C₆alkylthio; a group SR₁; C₁-C₆alkylamino; halo-C₁-C₆alkylamino; di-C₁-C₆alkylamino, in which the two alkyl groups are the same or different or, taken together, form, together with the

nitrogen atom, to which they are attached, a ring containing 1 ring nitrogen atom and 2 to 12 ring carbon atoms and optionally 1 further ring hetero atom, which then replaces 1 ring carbon atom and is selected from the group, consisting of an oxygen, a sulfur and a nitrogen atom, which ring is unsubstituted or substituted independently by 1 to 4 substituents, selected from the group, consisting of cyano, nitro, halogen, C₁-C₄alkyl and C₁-C₄alkoxy; di-(halo-C₁-C₆alkyl)-amino, in which the two haloalkyl groups are the same or different; C₃-C₆cycloalkylamino; N-(C₁-C₆alkyl)-N-(C₃-C₆cycloalkyl)-amino; or a group NHR₁, which group is optionally further substituted at the nitrogen atom by C₁-C₆alkyl or halo-C₁-C₆alkyl;

R₃ is hydrogen; a C₁-C₆alkyl, C₂-C₆alkenyl, C₂-C₆alkynyl or C₃-C₆cycloalkyl group, which group is unsubstituted or substituted independently by one or more substituents, selected from the group, consisting of the substituents R_a; C₁-C₆alkoxy; halo-C₁-C₆alkoxy; C₃-C₆cycloalkoxy; C₁-C₆alkylthio; halo-C₁-C₆alkylthio; C₁-C₆alkylamino; halo-C₁-C₆alkylamino; di-C₁-C₆alkylamino, in which the two alkyl groups are the same or different or, taken together, form, together with the nitrogen atom, to which they are attached, a ring containing 1 ring nitrogen atom and 2 to 12 ring carbon atoms and optionally 1 further ring hetero atom, which then replaces 1 ring carbon atom and is selected from the group, consisting of an oxygen, a sulfur and a nitrogen atom, which ring is unsubstituted or substituted independently by 1 to 4 substituents, selected from the group, consisting of cyano, nitro, halogen, C₁-C₄alkyl and C₁-C₄alkoxy; di-(halo-C₁-C₆alkyl)-amino, in which the two haloalkyl groups are the same or different; C₃-C₆cycloalkylamino; N-(C₁-C₆alkyl)-N-(C₃-C₆cycloalkyl)-amino; C₁-C₆alkoxycarbonyl; halo-C₁-C₆alkoxycarbonyl; C₁-C₆alkylcarbonyl or halo-C₁-C₆alkylcarbonyl;

R₄ is hydrogen; a substituent R₁; a substituent R_e; a C₁-C₆alkyl, C₂-C₆alkenyl, C₂-C₆alkynyl or C₃-C₆cycloalkyl group, which group is unsubstituted or substituted independently by one or more substituents, selected from the group, consisting of the substituents R_a, the substituents R_e and a phenyl, benzoyl, phenoxy or monocyclic or bicyclic heteroaryl group, which group is unsubstituted or substituted independently by 1 to 4 substituents, selected from the group, consisting of the substituents R_c; a group CH₂OR₁; a group CH₂SR₁; a group CH₂NHR₁, which group is optionally further substituted at the nitrogen atom by C₁-C₆alkyl or halo-C₁-C₆alkyl; C₁-C₆alkoxy; halo-C₁-C₆alkoxy; C₃-C₆cycloalkoxy; a group OR₁; C₁-C₆alkylthio; halo-C₁-C₆alkylthio; a group SR₁; C₁-C₆alkylsulfinyl; halo-C₁-C₆alkylsulfinyl; C₁-C₆alkylsulfonyl; halo-C₁-C₆alkylsulfonyl; C₁-C₆alkylamino; halo-C₁-C₆alkylamino; di-C₁-C₆alkylamino, in which the two alkyl groups are the same or different or, taken together, form, together with the nitrogen atom, to which they are attached, a ring containing 1 ring nitrogen

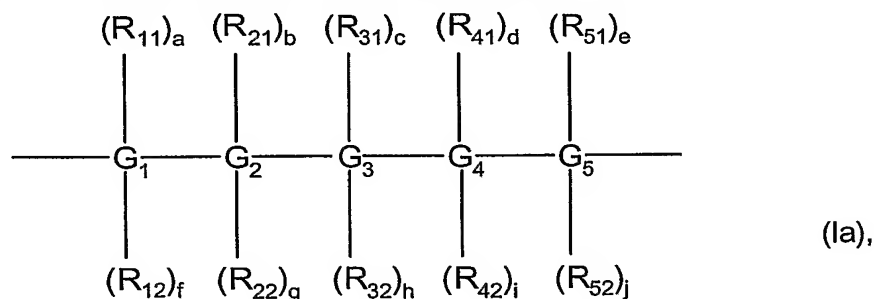
atom and 2 to 12 ring carbon atoms and optionally 1 further ring hetero atom, which then replaces 1 ring carbon atom and is selected from the group, consisting of an oxygen, a sulfur and a nitrogen atom, which ring is unsubstituted or substituted independently by 1 to 4 substituents, selected from the group, consisting of cyano, nitro, halogen, C₁-C₄alkyl and C₁-C₄alkoxy; di-(halo-C₁-C₆alkyl)-amino, in which the two haloalkyl groups are the same or different; C₃-C₆cycloalkylamino; N-(C₁-C₆alkyl)-N-(C₃-C₆cycloalkyl)-amino; a group NHR₁, which group is optionally further substituted at the nitrogen atom by C₁-C₆alkyl or halo-C₁-C₆alkyl; a group C(=O)R_d; a group C(=O)R_e; a group C(=S)R_d; or a group C(=S)R_e;

R_e is a carbocyclyl or heterocyclyl group, which group is monocyclic or bicyclic and is non-aromatic, in which group 1 or 2 of the ring members are optionally selected from the group, consisting of the groups C(=O), S(=O) and S(=O)₂, and which group is unsubstituted or substituted independently by 1 to 4 substituents, selected from the group, consisting of cyano, nitro, halogen, C₁-C₄alkyl and C₁-C₄alkoxy;

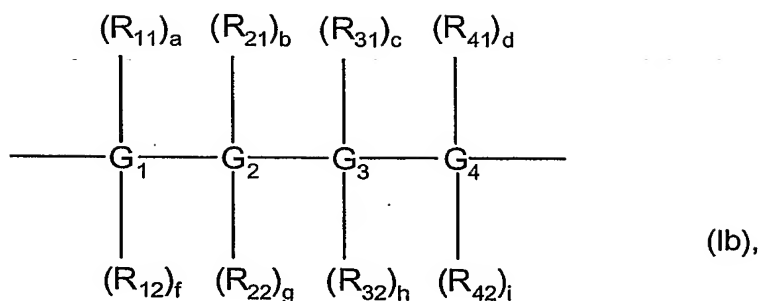
or R₃ and R₄, taken together, form, together with the nitrogen atom, to which they are attached, a ring containing 1 ring nitrogen atom and 2 to 6 ring carbon atoms and optionally 1 further ring hetero atom, which then replaces 1 ring carbon atom and is selected from the group, consisting of an oxygen, a sulfur and a nitrogen atom, which ring is unsubstituted or substituted independently by 1 to 4 substituents, selected from the group, consisting of cyano, nitro, halogen, C₁-C₄alkyl and C₁-C₄alkoxy;

R₅ is hydrogen; C₁-C₆alkyl; or halo-C₁-C₆alkyl; or has one of the meanings defined hereinafter;

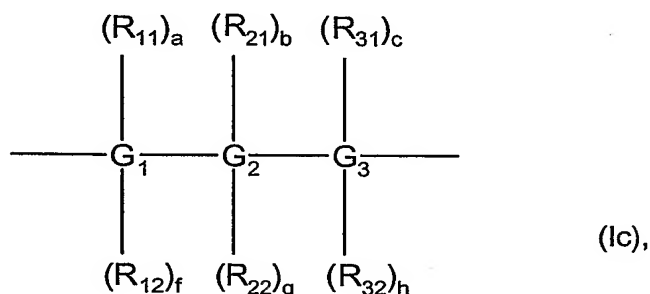
R₆ and R₇, taken together, are either a group of the formula



in which G₁ is attached to the carbon atom, shown in the formula I, that carries R₅; and in which G₅ is attached to the carbon atom, shown in the formula I, that carries R₈; or are a group of the formula



in which G_1 is attached to the carbon atom, shown in the formula I, that carries R_5 ; and in which G_4 is attached to the carbon atom, shown in the formula I, that carries R_8 ; or are a group of the formula



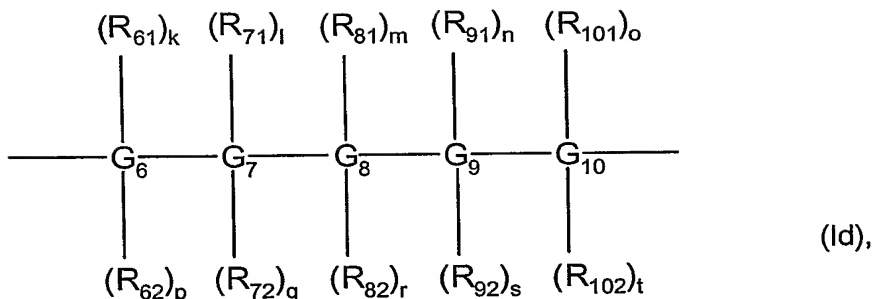
in which G_1 is attached to the carbon atom, shown in the formula I, that carries R_5 ; and in which G_3 is attached to the carbon atom, shown in the formula I, that carries R_8 ;

in which formulae 1a, 1b and 1c either a is 0; f is 0; and G_1 is a group C(=O); a group C(=S); an oxygen atom; a sulfur atom; a group S(=O); or a group S(=O)₂; or a is 0; f is 1; and G_1 is a nitrogen atom; or a is 1; f is 1; and G_1 is a carbon atom; either b is 0; g is 0; and G_2 is a group C(=O); a group C(=S); an oxygen atom; a sulfur atom; a group S(=O); or a group S(=O)₂; or b is 0; g is 1; and G_2 is a nitrogen atom; or b is 1; g is 1; and G_2 is a carbon atom; and either c is 0; h is 0; and G_3 is a group C(=O); a group C(=S); an oxygen atom; a sulfur atom; a group S(=O); or a group S(=O)₂; or c is 0; h is 1; and G_3 is a nitrogen atom; or c is 1; h is 1; and G_3 is a carbon atom;

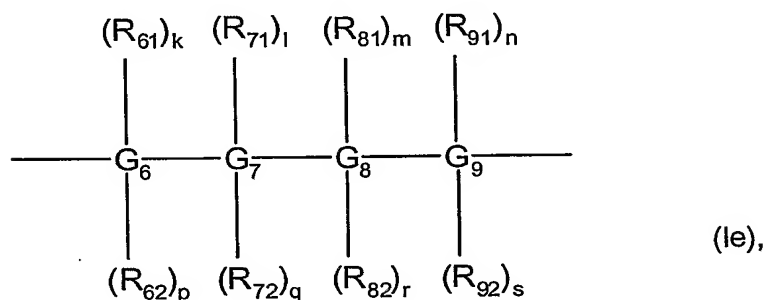
in which formulae 1a and 1b either d is 0; i is 0; and G_4 is a group C(=O); a group C(=S); an oxygen atom; a sulfur atom; a group S(=O); or a group S(=O)₂; or d is 0; i is 1; and G_4 is a nitrogen atom; or d is 1; i is 1; and G_4 is a carbon atom;

in which formula 1a either e is 0; j is 0; and G_5 is a group C(=O); a group C(=S); an oxygen atom; a sulfur atom; a group S(=O); or a group S(=O)₂; or e is 0; j is 1; and G_5 is a nitrogen atom; or e is 1; j is 1; and G_5 is a carbon atom;

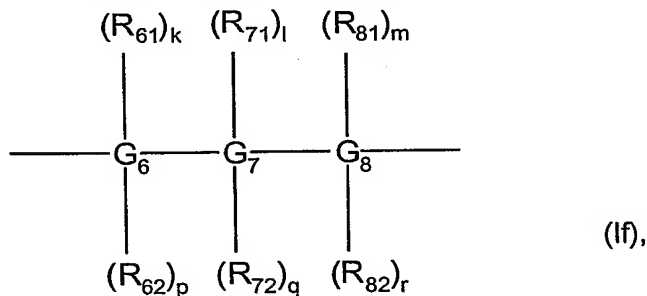
in which formula 1a either f is 1; g is 1; and R_{12} and R_{22} , taken together, are either a group of the formula



in which G_6 is attached to G_1 ; and in which G_{10} is attached to G_2 ; or are a group of the formula



in which G_6 is attached to G_1 ; and in which G_9 is attached to G_2 ; or are a group of the formula



in which G_6 is attached to G_1 ; and in which G_8 is attached to G_2 ;

or g is 1; h is 1; and R_{22} and R_{32} , taken together, are either a group of the formula Id, in which G_6 is attached to G_2 ; and in which G_{10} is attached to G_3 ; or are a group of the formula Ie, in which G_6 is attached to G_2 ; and in which G_9 is attached to G_3 ; or are a group of the formula If, in which G_6 is attached to G_2 ; and in which G_8 is attached to G_3 ;

or h is 1; i is 1; and R_{32} and R_{42} , taken together, are either a group of the formula Id, in which G_6 is attached to G_3 ; and in which G_{10} is attached to G_4 ; or are a group of the formula Ie, in which G_6 is attached to G_3 ; and in which G_9 is attached to G_4 ; or are a group of the formula If, in which G_6 is attached to G_3 ; and in which G_8 is attached to G_4 ;

or i is 1; j is 1; and R_{42} and R_{52} , taken together, are either a group of the formula Id, in which G_6 is attached to G_4 ; and in which G_{10} is attached to G_5 ; or are a group of the formula Ie, in

which G_6 is attached to G_4 ; and in which G_9 is attached to G_5 ; or are a group of the formula If, in which G_6 is attached to G_4 ; and in which G_8 is attached to G_5 ;

in which formula Ib either f is 1; g is 1; and R_{12} and R_{22} , taken together, are either a group of the formula Id, in which G_6 is attached to G_1 ; and in which G_{10} is attached to G_2 ; or are a group of the formula Ie, in which G_6 is attached to G_1 ; and in which G_9 is attached to G_2 ; or are a group of the formula If, in which G_6 is attached to G_1 ; and in which G_8 is attached to G_2 ;

or g is 1; h is 1; and R_{22} and R_{32} , taken together, are either a group of the formula Id, in which G_6 is attached to G_2 ; and in which G_{10} is attached to G_3 ; or are a group of the formula Ie, in which G_6 is attached to G_2 ; and in which G_9 is attached to G_3 ; or are a group of the formula If, in which G_6 is attached to G_2 ; and in which G_8 is attached to G_3 ;

or h is 1; i is 1; and R_{32} and R_{42} , taken together, are either a group of the formula Id, in which G_6 is attached to G_3 ; and in which G_{10} is attached to G_4 ; or are a group of the formula Ie, in which G_6 is attached to G_3 ; and in which G_9 is attached to G_4 ; or are a group of the formula If, in which G_6 is attached to G_3 ; and in which G_8 is attached to G_4 ;

in which formula Ic either f is 1; g is 1; and R_{12} and R_{22} , taken together, are either a group of the formula Id, in which G_6 is attached to G_1 ; and in which G_{10} is attached to G_2 ; or are a group of the formula Ie, in which G_6 is attached to G_1 ; and in which G_9 is attached to G_2 ; or are a group of the formula If, in which G_6 is attached to G_1 ; and in which G_8 is attached to G_2 ;

or g is 1; h is 1; and R_{22} and R_{32} , taken together, are either a group of the formula Id, in which G_6 is attached to G_2 ; and in which G_{10} is attached to G_3 ; or are a group of the formula Ie, in which G_6 is attached to G_2 ; and in which G_9 is attached to G_3 ; or are a group of the formula If, in which G_6 is attached to G_2 ; and in which G_8 is attached to G_3 ;

in which formulae Ia, Ib and Ic the atoms G_1 and G_2 can be connected by one additional bond, which bond, if present, is represented by a first substituent, which is R_{12} , if G_1 is a nitrogen atom, and which is R_{11} or R_{12} , if G_1 is a carbon atom, and a second substituent, which is R_{22} , if G_2 is a nitrogen atom, and which is R_{21} or R_{22} , if G_2 is a carbon atom, taken together;

in which formulae Ia, Ib and Ic the atoms G_2 and G_3 can be connected by one additional bond, which bond, if present, is represented by a first substituent, which is R_{22} , if G_2 is a nitrogen atom, and which is R_{21} or R_{22} , if G_2 is a carbon atom, and a second substituent, which is R_{32} , if G_3 is a nitrogen atom, and which is R_{31} or R_{32} , if G_3 is a carbon atom, taken together;

in which formulae Ia and Ib the atoms G_3 and G_4 can be connected by one additional bond, which bond, if present, is represented by a first substituent, which is R_{32} , if G_3 is a nitrogen atom, and which is R_{31} or R_{32} , if G_3 is a carbon atom, and a second substituent, which is R_{42} , if G_4 is a nitrogen atom, and which is R_{41} or R_{42} , if G_4 is a carbon atom, taken together;

in which formula Ia the atoms G_4 and G_5 can be connected by one additional bond, which bond, if present, is represented by a first substituent, which is R_{42} , if G_4 is a nitrogen atom, and which is R_{41} or R_{42} , if G_4 is a carbon atom, and a second substituent, which is R_{52} , if G_5 is a nitrogen atom, and which is R_{51} or R_{52} , if G_5 is a carbon atom, taken together;

in which formulae Ia, Ib and Ic the atom G_1 can be connected with the carbon atom, shown in the formula I, that carries R_5 , by one additional bond, which bond, if present, is represented by a first substituent, which is R_{12} , if G_1 is a nitrogen atom, and which is R_{11} or R_{12} , if G_1 is a carbon atom, and a second substituent, which is R_5 , taken together;

in which formula Ia the atom G_5 can be connected with the carbon atom, shown in the formula I, that carries R_8 , by one additional bond, which bond, if present, is represented by a first substituent, which is R_{52} , if G_5 is a nitrogen atom, and which is R_{51} or R_{52} , if G_5 is a carbon atom, and a second substituent, which is R_8 , taken together;

in which formula Ib the atom G_4 can be connected with the carbon atom, shown in the formula I, that carries R_8 , by one additional bond, which bond, if present, is represented by a first substituent, which is R_{42} , if G_4 is a nitrogen atom, and which is R_{41} or R_{42} , if G_4 is a carbon atom, and a second substituent, which is R_8 , taken together;

in which formula Ic the atom G_3 can be connected with the carbon atom, shown in the formula I, that carries R_8 , by one additional bond, which bond, if present, is represented by a first substituent, which is R_{32} , if G_3 is a nitrogen atom, and which is R_{31} or R_{32} , if G_3 is a carbon atom, and a second substituent, which is R_8 , taken together;

in which formula Ia each of those substituents, selected from the group, consisting of the substituents R_{11} , R_{12} , R_{21} , R_{22} , R_{31} , R_{32} , R_{41} , R_{42} , R_{51} and R_{52} , which are different from the two substituents, which, taken together, form the group of the formula Id, Ie or If, and different from any first substituent, if present, as defined hereinbefore for the formula Ia, and from any second substituent, if present, as defined hereinbefore for the formula Ia, is independently selected from the group, consisting of the substituents R_i ;

in which formula Ib each of those substituents, selected from the group, consisting of the substituents R_{11} , R_{12} , R_{21} , R_{22} , R_{31} , R_{32} , R_{41} and R_{42} , which are different from the two substituents, which, taken together, form the group of the formula Id, Ie or If, and different from

any first substituent, if present, as defined hereinbefore for the formula Ib, and from any second substituent, if present, as defined hereinbefore for the formula Ib, is independently selected from the group, consisting of the substituents R_f ;

in which formula Ic each of those substituents, selected from the group, consisting of the substituents R_{11} , R_{12} , R_{21} , R_{22} , R_{31} and R_{32} , which are different from the two substituents, which, taken together, form the group of the formula Id, Ie or If, and different from any first substituent, if present, as defined hereinbefore for the formula Ic, and from any second substituent, if present, as defined hereinbefore for the formula Ic, is independently selected from the group, consisting of the substituents R_f ;

R_f is hydrogen; or a substituent R_g ; the total number of the substituents R_g , if present, having an upper limit of 5 for a group of the formula Ia; of 4 for a group of the formula Ib; and of 3 for a group of the formula Ic; which total number can, however, be limited for a specific group of the formula Ia, Ib or Ic to a value lower than the upper limit mentioned hereinbefore, which value is then equal to the number of the positions available for the substitution by a substituent R_g in this specific group;

R_g is either attached to a carbon atom and then selected from the group, consisting of the substituents R_{g-c} ; or attached to a nitrogen atom and then selected from the group, consisting of the substituents R_{g-n} ;

R_{g-c} is a substituent R_c ;

R_{g-n} is cyano; nitro; C_1 - C_6 alkyl; halo- C_1 - C_6 alkyl; C_1 - C_6 alkoxy- C_1 - C_6 alkyl; C_2 - C_6 alkenyl; halo- C_2 - C_6 alkenyl; C_2 - C_6 alkynyl; halo- C_2 - C_6 alkynyl; C_3 - C_6 cycloalkyl; halo- C_3 - C_6 cycloalkyl; C_1 - C_6 alkoxy; halo- C_1 - C_6 alkoxy; C_3 - C_6 cycloalkoxy; C_1 - C_6 alkylthio; halo- C_1 - C_6 alkylthio; C_1 - C_6 alkylsulfinyl; halo- C_1 - C_6 alkylsulfinyl; C_1 - C_6 alkylsulfonyl; halo- C_1 - C_6 alkylsulfonyl; amino; C_1 - C_6 alkylamino; halo- C_1 - C_6 alkylamino; di- C_1 - C_6 alkylamino, in which the two alkyl groups are the same or different or, taken together, form, together with the nitrogen atom, to which they are attached, a ring containing 1 ring nitrogen atom and 2 to 12 ring carbon atoms and optionally 1 further ring hetero atom, which then replaces 1 ring carbon atom and is selected from the group, consisting of an oxygen, a sulfur and a nitrogen atom, which ring is unsubstituted or substituted independently by 1 to 4 substituents, selected from the group, consisting of cyano, nitro, halogen, C_1 - C_4 alkyl and C_1 - C_4 alkoxy; di-(halo- C_1 - C_6 alkyl)-amino, in which the two haloalkyl groups are the same or different; C_3 - C_6 cycloalkylamino; N-(C_1 - C_6 alkyl)-N-(C_3 - C_6 cycloalkyl)-amino; C_1 - C_6 alkoxycarbonyl; halo- C_1 - C_6 alkoxycarbonyl; aminocarbonyl; C_1 - C_6 alkylaminocarbonyl; halo- C_1 - C_6 alkylaminocarbonyl; di- C_1 - C_6 alkylaminocarbonyl, in which the two alkyl groups are the same or different or, taken together, form, together with the

nitrogen atom, to which they are attached, a ring containing 1 ring nitrogen atom and 2 to 12 ring carbon atoms and optionally 1 further ring hetero atom, which then replaces 1 ring carbon atom and is selected from the group, consisting of an oxygen, a sulfur and a nitrogen atom, which ring is unsubstituted or substituted independently by 1 to 4 substituents, selected from the group, consisting of cyano, nitro, halogen, C₁-C₄alkyl and C₁-C₄alkoxy; di-(halo-C₁-C₆alkyl)-aminocarbonyl, in which the two haloalkyl groups are the same or different; C₁-C₆alkylcarbonyl; halo-C₁-C₆alkylcarbonyl; tri-C₁-C₆alkylsilyl, in which the three alkyl groups are the same or different; or a phenyl, benzyl, benzoyl, phenoxy or monocyclic or bicyclic heteroaryl group, which group is unsubstituted or substituted independently by 1 to 4 substituents, selected from the group, consisting of the substituents R_a;

in which formulae Id, le and lf either k is 0; p is 0; and G₆ is a group C(=O); a group C(=S); an oxygen atom; a sulfur atom; a group S(=O); or a group S(=O)₂; or k is 0; p is 1; and G₆ is a nitrogen atom; or k is 1; p is 1; and G₆ is a carbon atom; either l is 0; q is 0; and G₇ is a group C(=O); a group C(=S); an oxygen atom; a sulfur atom; a group S(=O); or a group S(=O)₂; or l is 0; q is 1; and G₇ is a nitrogen atom; or l is 1; q is 1; and G₇ is a carbon atom; and either m is 0; r is 0; and G₈ is a group C(=O); a group C(=S); an oxygen atom; a sulfur atom; a group S(=O); or a group S(=O)₂; or m is 0; r is 1; and G₈ is a nitrogen atom; or m is 1; r is 1; and G₈ is a carbon atom;

in which formulae Id and le either n is 0; s is 0; and G₉ is a group C(=O); a group C(=S); an oxygen atom; a sulfur atom; a group S(=O); or a group S(=O)₂; or n is 0; s is 1; and G₉ is a nitrogen atom; or n is 1; s is 1; and G₉ is a carbon atom;

in which formula Id either o is 0; t is 0; and G₁₀ is a group C(=O); a group C(=S); an oxygen atom; a sulfur atom; a group S(=O); or a group S(=O)₂; or o is 0; t is 1; and G₁₀ is a nitrogen atom; or o is 1; t is 1; and G₁₀ is a carbon atom;

in which formulae Id, le and lf the atoms G₆ and G₇ can be connected by one additional bond, which bond, if present, is represented by a first substituent, which is R₆₂, if G₆ is a nitrogen atom, and which is R₆₁ or R₆₂, if G₆ is a carbon atom, and a second substituent, which is R₇₂, if G₇ is a nitrogen atom, and which is R₇₁ or R₇₂, if G₇ is a carbon atom, taken together;

in which formulae Id, le and lf the atoms G₇ and G₈ can be connected by one additional bond, which bond, if present, is represented by a first substituent, which is R₇₂, if G₇ is a nitrogen atom, and which is R₇₁ or R₇₂, if G₇ is a carbon atom, and a second substituent, which is R₈₂, if G₈ is a nitrogen atom, and which is R₈₁ or R₈₂, if G₈ is a carbon atom, taken together;

in which formulae Id and Ie the atoms G_8 and G_9 can be connected by one additional bond, which bond, if present, is represented by a first substituent, which is R_{82} , if G_8 is a nitrogen atom, and which is R_{81} or R_{82} , if G_8 is a carbon atom, and a second substituent, which is R_{92} , if G_9 is a nitrogen atom, and which is R_{91} or R_{92} , if G_9 is a carbon atom, taken together;

in which formula Id the atoms G_9 and G_{10} can be connected by one additional bond, which bond, if present, is represented by a first substituent, which is R_{92} , if G_9 is a nitrogen atom, and which is R_{91} or R_{92} , if G_9 is a carbon atom, and a second substituent, which is R_{102} , if G_{10} is a nitrogen atom, and which is R_{101} or R_{102} , if G_{10} is a carbon atom, taken together;

in which formulae Id, Ie and If the atom G_6 can be connected either with the atom G_1 , shown in the formulae Ia, Ib and Ic, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{62} , if G_6 is a nitrogen atom, and which is R_{61} or R_{62} , if G_6 is a carbon atom, and a second substituent, which is R_{12} , if G_1 is a nitrogen atom, and which is R_{11} or R_{12} , if G_1 is a carbon atom, taken together;

or with the atom G_2 , shown in the formulae Ia, Ib and Ic, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{62} , if G_6 is a nitrogen atom, and which is R_{61} or R_{62} , if G_6 is a carbon atom, and a second substituent, which is R_{22} , if G_2 is a nitrogen atom, and which is R_{21} or R_{22} , if G_2 is a carbon atom, taken together;

or with the atom G_3 , shown in the formulae Ia and Ib, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{62} , if G_6 is a nitrogen atom, and which is R_{61} or R_{62} , if G_6 is a carbon atom, and a second substituent, which is R_{32} , if G_3 is a nitrogen atom, and which is R_{31} or R_{32} , if G_3 is a carbon atom, taken together;

or with the atom G_4 , shown in the formula Ia, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{62} , if G_6 is a nitrogen atom, and which is R_{61} or R_{62} , if G_6 is a carbon atom, and a second substituent, which is R_{42} , if G_4 is a nitrogen atom, and which is R_{41} or R_{42} , if G_4 is a carbon atom, taken together;

in which formula Id the atom G_{10} can be connected either with the atom G_2 , shown in the formulae Ia, Ib and Ic, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{102} , if G_{10} is a nitrogen atom, and which is R_{101} or R_{102} , if G_{10} is a carbon atom, and a second substituent, which is R_{22} , if G_2 is a nitrogen atom, and which is R_{21} or R_{22} , if G_2 is a carbon atom, taken together;

or with the atom G_3 , shown in the formulae Ia, Ib and Ic, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{102} , if G_{10} is a nitrogen atom, and

which is R_{101} or R_{102} , if G_{10} is a carbon atom, and a second substituent, which is R_{32} , if G_3 is a nitrogen atom, and which is R_{31} or R_{32} , if G_3 is a carbon atom, taken together;
or with the atom G_4 , shown in the formulae Ia and Ib, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{102} , if G_{10} is a nitrogen atom, and which is R_{101} or R_{102} , if G_{10} is a carbon atom, and a second substituent, which is R_{42} , if G_4 is a nitrogen atom, and which is R_{41} or R_{42} , if G_4 is a carbon atom, taken together;
or with the atom G_5 , shown in the formula Ia, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{102} , if G_{10} is a nitrogen atom, and which is R_{101} or R_{102} , if G_{10} is a carbon atom, and a second substituent, which is R_{52} , if G_5 is a nitrogen atom, and which is R_{51} or R_{52} , if G_5 is a carbon atom, taken together;

in which formula Ib the atom G_9 can be connected either with the atom G_2 , shown in the formulae Ia, Ib and Ic, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{92} , if G_9 is a nitrogen atom, and which is R_{91} or R_{92} , if G_9 is a carbon atom, and a second substituent, which is R_{22} , if G_2 is a nitrogen atom, and which is R_{21} or R_{22} , if G_2 is a carbon atom, taken together;
or with the atom G_3 , shown in the formulae Ia, Ib and Ic, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{92} , if G_9 is a nitrogen atom, and which is R_{91} or R_{92} , if G_9 is a carbon atom, and a second substituent, which is R_{32} , if G_3 is a nitrogen atom, and which is R_{31} or R_{32} , if G_3 is a carbon atom, taken together;
or with the atom G_4 , shown in the formulae Ia and Ib, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{92} , if G_9 is a nitrogen atom, and which is R_{91} or R_{92} , if G_9 is a carbon atom, and a second substituent, which is R_{42} , if G_4 is a nitrogen atom, and which is R_{41} or R_{42} , if G_4 is a carbon atom, taken together;
or with the atom G_5 , shown in the formula Ia, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{92} , if G_9 is a nitrogen atom, and which is R_{91} or R_{92} , if G_9 is a carbon atom, and a second substituent, which is R_{52} , if G_5 is a nitrogen atom, and which is R_{51} or R_{52} , if G_5 is a carbon atom, taken together;

in which formula Ic the atom G_8 can be connected either with the atom G_2 , shown in the formulae Ia, Ib and Ic, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{82} , if G_8 is a nitrogen atom, and which is R_{81} or R_{82} , if G_8 is a carbon atom, and a second substituent, which is R_{22} , if G_2 is a nitrogen atom, and which is R_{21} or R_{22} , if G_2 is a carbon atom, taken together;
or with the atom G_3 , shown in the formulae Ia, Ib and Ic, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{82} , if G_8 is a nitrogen atom, and which

is R_{81} or R_{82} , if G_8 is a carbon atom, and a second substituent, which is R_{32} , if G_3 is a nitrogen atom, and which is R_{31} or R_{32} , if G_3 is a carbon atom, taken together;
or with the atom G_4 , shown in the formulae Ia and Ib, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{82} , if G_8 is a nitrogen atom, and which is R_{81} or R_{82} , if G_8 is a carbon atom, and a second substituent, which is R_{42} , if G_4 is a nitrogen atom, and which is R_{41} or R_{42} , if G_4 is a carbon atom, taken together;
or with the atom G_5 , shown in the formula Ia, by one additional bond, which bond, if present, is represented by a first substituent, which is R_{82} , if G_8 is a nitrogen atom, and which is R_{81} or R_{82} , if G_8 is a carbon atom, and a second substituent, which is R_{52} , if G_5 is a nitrogen atom, and which is R_{51} or R_{52} , if G_5 is a carbon atom, taken together;

in which formula Id each of those substituents, selected from the group, consisting of the substituents R_{61} , R_{62} , R_{71} , R_{72} , R_{81} , R_{82} , R_{91} , R_{92} , R_{101} and R_{102} , which are different from any first substituent, if present, as defined hereinbefore for the formula Id, and from any second substituent, if present, as defined hereinbefore for the formula Id, is independently selected from the group, consisting of the substituents R_h ;

in which formula Ie each of those substituents, selected from the group, consisting of the substituents R_{61} , R_{62} , R_{71} , R_{72} , R_{81} , R_{82} , R_{91} and R_{92} , which are different from any first substituent, if present, as defined hereinbefore for the formula Ie, and from any second substituent, if present, as defined hereinbefore for the formula Ie, is independently selected from the group, consisting of the substituents R_i ;

in which formula If each of those substituents, selected from the group, consisting of the substituents R_{61} , R_{62} , R_{71} , R_{72} , R_{81} and R_{82} , which are different from any first substituent, if present, as defined hereinbefore for the formula If, and from any second substituent, if present, as defined hereinbefore for the formula If, is independently selected from the group, consisting of the substituents R_h ;

R_h is hydrogen; or a substituent R_j ; the total number of the substituents R_j , if present, having an upper limit of 6 for a group of the formula Id; and of 4 for a group of the formula If; which total number can, however, be limited for a specific group of the formula Id or If to a value lower than the upper limit mentioned hereinbefore, which value is then equal to the number of the positions available for the substitution by a substituent R_j in this specific group;

R_i is hydrogen; or a substituent R_k ; the total number of the substituents R_k , if present, having an upper limit of 5; which total number can, however, be limited for a specific group of the formula Ie to a value lower than the upper limit mentioned hereinbefore, which value is

then equal to the number of the positions available for the substitution by a substituent R_k in this specific group;

R_j is either attached to a carbon atom and then selected from the group, consisting of the substituents R_{j-c} ; or attached to a nitrogen atom and then selected from the group, consisting of the substituents R_{j-n} ;

R_{j-c} is a substituent R_c ;

R_{j-n} is a substituent R_{g-n} ;

R_k is either attached to a carbon atom and then selected from the group, consisting of the substituents R_{k-c} ; or attached to a nitrogen atom and then selected from the group, consisting of the substituents R_{k-n} ;

or 2 substituents R_k , the first of which is attached to the atom G_6 and is represented by R_{62} , if G_6 is a nitrogen atom, and by R_{61} or R_{62} , if G_6 is a carbon atom, and the second of which is attached to the atom G_9 and is represented by R_{92} , if G_9 is a nitrogen atom, and by R_{91} or R_{92} , if G_9 is a carbon atom, taken together, are $-CH_2-$; or $-O-$;

R_{k-c} is a substituent R_c ;

R_{k-n} is a substituent R_{g-n} ;

R_8 is hydrogen; C_1 - C_6 alkyl; or halo- C_1 - C_6 alkyl; or has one of the meanings defined hereinbefore or hereinafter;

or R_5 and R_8 , taken together, are a bond;

with the proviso, that

(i) a ring oxygen atom, if present, is not directly connected with a further ring oxygen atom, if any;

(ii) a ring carbon atom, selected from the group, consisting of G_1 , G_2 , G_3 , G_4 , G_5 , G_6 , G_7 , G_8 , G_9 and G_{10} , is, if present, not directly connected with any other atom by a triple bond or with any other 2 different atoms by 2 double bonds;

(iii) not more than 6 of the variables G_1 , G_2 , G_3 , G_4 , G_5 , G_6 , G_7 , G_8 , G_9 and G_{10} can, if present, be selected from the group, consisting of an oxygen atom, a sulfur atom, a group $S(=O)$, a group $S(=O)_2$ and a nitrogen atom, each of the remaining of these variables, if any, being selected from the group, consisting of a carbon atom, a group $C(=O)$ and a group $C(=S)$, and not more than 3 of the said 6 variables can be selected from the group, consisting of an oxygen atom, a sulfur atom, a group $S(=O)$ and a group $S(=O)_2$; and

(iv) unless otherwise defined hereinbefore, the meaning of a variable at a certain occurrence can be selected independently from the meaning of the same variable at any other occurrence, if any.

Unless otherwise defined, the general terms used hereinabove and hereinbelow have the meanings which follow.

Halogen - as a group per se and as a structural element of other groups and compounds, such as haloalkyl - is, for example, fluorine, chlorine, bromine or iodine, in particular fluorine, chlorine or bromine, but especially chlorine or bromine.

Unless otherwise defined, carbon-containing groups and compounds comprise for example in each case 1 up to and including 15, preferably 1 up to and including 10, especially 1 up to and including 8, in particular 1 up to and including 5, especially 1 or 2, carbon atom(s).

Cycloalkyl - as a group per se and as a structural element of other groups and compounds, such as halocycloalkyl - is, in each case with due consideration of the number of carbon atoms contained in each case in the relevant group or compound, for example cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.

Alkyl - as a group per se and as a structural element of other groups and compounds, such as haloalkyl - is, in each case with due consideration of the number of carbon atoms contained in each case in the relevant group or compound, either straight-chain, for example methyl, ethyl, propyl, butyl, pentyl or hexyl, or branched, for example isopropyl, isobutyl, sec-butyl, tert-butyl, isopentyl, neopentyl or isohexyl.

Alkenyl - as a group per se and as a structural element of other groups and compounds, such as haloalkenyl - is, in each case with due consideration of the number of carbon atoms contained in each case in the relevant group or compound, either straight-chain or branched and comprises in each case 2 or more than 2 or preferably 1 carbon-carbon double bond(s), the double bonds of these substituents being separated from the remaining moiety of the compound I by preferably at least one saturated carbon atom, and is, for example, allyl, propen-2-yl, methallyl, but-2-en-1-yl, but-3-en-1-yl or pent-4-en-1-yl.

Alkynyl - as a group per se and as a structural element of other groups and compounds, such as haloalkynyl - is, in each case with due consideration of the number of carbon atoms contained in each case in the relevant group or compound, either straight-chain or branched

and comprises in each case 2 or more than 2 or preferably 1 carbon-carbon triple bond(s), the triple bonds of these substituents being separated from the remaining moiety of the compound I by preferably at least one saturated carbon atom, and is, for example, propargyl, but-2-ynyl or but-3-yn-2-yl.

Aryl is, for example, naphthyl or, preferably, phenyl.

Heteroaryl has, for example, an aromatic ring skeleton composed of a ring having 5 or 6 ring members or of a combination of at least two rings having in each case independently of one another 5 or 6 ring members, where for example 1 up to and including 4 of the ring members is (are) (a) heteroatom(s) selected from the group consisting of nitrogen, oxygen and sulfur, and is, for example, pyridyl, thienyl, pyrazolyl, thiazolyl, thiadiazolyl, furyl, oxadiazolyl, indoliziny, pyrimidyl, quinolyl or pteridinyl.

Non-aromatic heterocyclyl has, for example, a non-aromatic ring skeleton composed of a ring having 5 or 6 ring members or of a combination of at least two rings having in each case independently of one another 5 or 6 ring members, where for example 1 up to and including 4 of the ring members is (are) (a) heteroatom(s) selected from the group consisting of nitrogen, oxygen and sulfur and is, for example, piperidyl, pyrrolinyl, tetrahydrofuryl or chromanyl.

Halogen-substituted carbon-containing groups and compounds, such as haloalkyl, can be partially halogenated or perhalogenated, where, in the case of polyhalogenation, the halogen substituents can be identical or different.

The following are further preferred embodiments within the scope of the invention:

(3) A compound according to (1) or (2) of the formula I, in which Z_1 is an oxygen atom;

(4) A compound according to any one of (1) to (3) of the formula I, in which Z_2 is an oxygen atom;

(5) A compound according to any one of (1) to (4) of the formula I, in which R_1 is a phenyl, pyridyl or pyrazolyl group, which is unsubstituted or preferably substituted;

especially a phenyl, pyridyl or pyrazolyl group, which is substituted independently by 1 to 3 substituents, selected from the group, consisting of halogen, C₁-C₆alkyl, halo-C₁-C₆alkyl, C₁-C₆alkoxy, halo-C₁-C₆alkoxy and a phenyl or pyridyl group, which group is unsubstituted or preferably substituted;

more especially a phenyl, pyridyl or pyrazolyl group, which is substituted independently by 1 to 3 substituents, selected from the group, consisting of halogen, C₁-C₆alkyl, halo-C₁-C₆alkyl, halo-C₁-C₆alkoxy and a phenyl or pyridyl group, which group is substituted independently by 1 to 3 substituents, selected from the group, consisting of halogen and C₁-C₆alkyl;

preferably a phenyl or pyridyl group, which is substituted independently by 1 to 3 substituents, selected from the group, consisting of C₁-C₆alkyl and halo-C₁-C₆alkyl; or a pyrazolyl group, which is substituted independently by 1 to 3 substituents, selected from the group, consisting of halogen, C₁-C₆alkyl, halo-C₁-C₆alkyl, halo-C₁-C₆alkoxy and a phenyl or pyridyl group, which group is substituted independently by 1 to 3 substituents, selected from the group, consisting of halogen and C₁-C₆alkyl;

more preferably a pyrazolyl group, which is substituted independently by 1 to 3 substituents, selected from the group, consisting of halogen, C₁-C₆alkyl, halo-C₁-C₆alkyl, halo-C₁-C₆alkoxy and a phenyl or pyridyl group, which group is substituted independently by 1 to 3 substituents, selected from the group, consisting of halogen and C₁-C₆alkyl;

especially a pyrazol-3-yl group, which is substituted independently by 1 to 3 substituents, selected from the group, consisting of halogen, C₁-C₆alkyl, halo-C₁-C₆alkyl, halo-C₁-C₆alkoxy and a phenyl or pyridyl group, which group is substituted independently by 1 to 3 substituents, selected from the group, consisting of halogen and C₁-C₆alkyl;

more especially a pyrazol-3-yl group, which is substituted independently by 1 to 3 substituents, selected from the group, consisting of halogen, halo-C₁-C₆alkyl, halo-C₁-C₆alkoxy and a phenyl or pyridyl group, which group is substituted independently by 1 to 3 substituents, selected from the group, consisting of halogen and C₁-C₆alkyl;

preferably a pyrazol-3-yl group, which is substituted independently by 1 to 3 substituents, selected from the group, consisting of halogen, halo-C₁-C₆alkyl, halo-C₁-C₆alkoxy and a pyridyl group, which group is substituted independently by 1 to 3 substituents, selected from the group, consisting of halogen;

more preferably a pyrazol-3-yl group, which is substituted independently by 1 to 3 substituents, selected from the group, consisting of halogen, halo-C₁-C₆alkyl, halo-C₁-C₆alkoxy and a pyrid-2-yl group, which group is substituted independently by 1 or 2 substituents, selected from the group, consisting of halogen;

especially a pyrazol-5-yl group, which is substituted in the 3-position by halogen, halo-C₁-C₆alkyl or halo-C₁-C₆alkoxy and in the 1-position by a pyrid-2-yl group, which group is substituted independently by 1 or 2 substituents, selected from the group, consisting of halogen;

more especially a pyrazol-5-yl group, which is substituted in the 3-position by halogen, halo-C₁-C₆alkyl or halo-C₁-C₆alkoxy and in the 1-position by a pyrid-2-yl group, which group is substituted in the 3-position by halogen;

preferably a pyrazol-5-yl group, which is substituted in the 3-position by halogen, halo-C₁-C₆alkyl or halo-C₁-C₆alkoxy and in the 1-position by a pyrid-2-yl group, which group is substituted in the 3-position by chlorine or bromine;

more preferably a pyrazol-5-yl group, which is substituted in the 3-position by halo-C₁-C₆alkyl and in the 1-position by a pyrid-2-yl group, which group is substituted in the 3-position by chlorine or bromine;

most preferably a pyrazol-5-yl group, which is substituted in the 3-position by trifluoromethyl and in the 1-position by a pyrid-2-yl group, which group is substituted in the 3-position by chlorine or bromine;

(6) A compound according to any one of (1) to (5) of the formula I, in which R₂ is hydrogen or C₁-C₆alkyl;
preferably hydrogen;

(7) A compound according to any one of (1) to (6) of the formula I, in which R₃ is hydrogen or C₁-C₆alkyl;
preferably hydrogen;

(8) A compound according to any one of (1) to (7) of the formula I, in which R₄ is C₁-C₆alkyl;
preferably methyl or isopropyl;

(9) A compound according to any one of (1) to (8) of the formula I, in which R₅ and R₈, taken together, are a bond;

(10) A compound according to any one of (1) to (9) of the formula I, in which R₆ and R₇, taken together, are a group of the formula Ib or a group of the formula Ic;

(11) A compound according to any one of (1) to (10) of the formula I, in which the two carbon atoms, shown in the formula I, to which atoms R_6 and R_7 are attached, are two ring members of an aromatic ring;

(12) A compound according to any one of (1) to (11) of the formula I, in which R_6 and R_7 , taken together, form, together with the two carbon atoms, shown in the formula I, to which atoms they are attached, and together with R_5 and with R_8 , one of the bicyclic ring systems shown in the formulae T1 to T71, each of which ring systems is substituted by the two substituents $-N(R_2)-C(=Z_1)-R_1$ and $-C(=Z_2)-N(R_3)-R_4$;

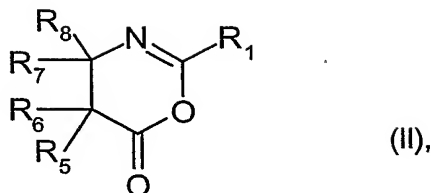
preferably taken together, form, together with the two carbon atoms, shown in the formula I, to which atoms they are attached, and together with R_5 and with R_8 , one of the bicyclic ring systems shown in the formulae T1, T6, T7, T21, T37 and T38, each of which ring systems is substituted by the two substituents $-N(R_2)-C(=Z_1)-R_1$ and $-C(=Z_2)-N(R_3)-R_4$;
more preferably taken together, form, together with the two carbon atoms, shown in the formula I, to which atoms they are attached, and together with R_5 and with R_8 , one of the bicyclic ring systems shown in the formulae T1 and T7, each of which ring systems is substituted by the two substituents $-N(R_2)-C(=Z_1)-R_1$ and $-C(=Z_2)-N(R_3)-R_4$.

Especially preferred within the scope of the invention are the compounds of the formula I mentioned in the Examples P3, P6 and P9 to P11.

Individually preferred within the scope of the invention is each of the compounds T1.1, T1.3, T6.1, T6.3, T7.1, T7.3, T21.3, T37.3 and T38.3.

As a further subject of the invention, the process for the preparation of a compound of the formula I or, where appropriate, a tautomer thereof, in each case in free form or in salt form, comprises, for example,

a) to prepare a compound of the formula I, in which Z_1 is an oxygen atom; Z_2 is an oxygen atom; and R_2 is hydrogen, or, where appropriate, a tautomer and/or salt thereof, reacting a compound of the formula



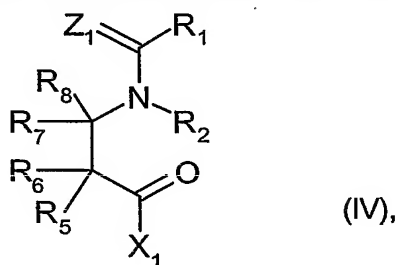
in which R_1 , R_5 , R_6 , R_7 and R_8 have the meanings given for the formula I, or, where appropriate, a tautomer and/or salt thereof with a compound of the formula



in which R_3 and R_4 have the meanings given for the formula I, or, where appropriate, with a tautomer and/or salt thereof or,

b) to prepare a compound of the formula I, in which Z_1 is a sulfur atom; and Z_2 is a sulfur atom, or, where appropriate, a tautomer and/or salt thereof, reacting a compound of the formula I, in which Z_1 is an oxygen atom; and Z_2 is an oxygen atom, or, where appropriate, a tautomer and/or salt thereof with a sulfurising agent or,

c) to prepare a compound of the formula I, in which Z_2 is an oxygen atom, or, where appropriate, a tautomer and/or salt thereof, reacting a compound of the formula

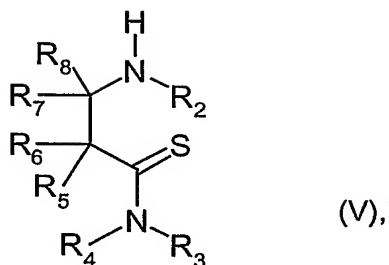


in which Z_1 , R_1 , R_2 , R_5 , R_6 , R_7 and R_8 have the meanings given for the formula I; and X_1 is a leaving group, or, where appropriate, a tautomer and/or salt thereof with a compound of the formula

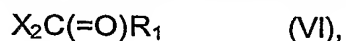


in which R_3 and R_4 have the meanings given for the formula I, or, where appropriate, with a tautomer and/or salt thereof or,

d) to prepare a compound of the formula I, in which Z_1 is an oxygen atom; and Z_2 is a sulfur atom, or, where appropriate, a tautomer and/or salt thereof, reacting a compound of the formula



in which R_2 , R_3 , R_4 , R_5 , R_6 , R_7 and R_8 have the meanings given for the formula I or, where appropriate, a tautomer and/or salt thereof with a compound of the formula



in which R_1 has the meaning given for the formula I; and X_2 is a leaving group, or, where appropriate, with a tautomer and/or salt thereof

and/or converting a compound of the formula I or, where appropriate, a tautomer thereof, in each case in free form or in salt form, into another compound of the formula I or, where appropriate, a tautomer thereof, separating an isomer mixture, which can be obtained in accordance with the process, and isolating the desired isomer and/or converting a free compound of the formula I or, where appropriate, a tautomer thereof into a salt or a salt of a compound of the formula I or, where appropriate, a tautomer thereof into the free compound of the formula I or, where appropriate, a tautomer thereof or into another salt.

What has been said above for tautomers and/or salts of compounds I applies analogously to starting materials mentioned hereinabove and hereinbelow with regard to the tautomers and/or salts thereof.

The reactions described hereinabove and hereinbelow are carried out in a manner known per se, for example in the absence or, normally, in the presence of a suitable solvent or diluent or of a mixture of these, the process being carried out, as required, with cooling, at room temperature or with heating, for example in a temperature range of from approximately -80°C to the boiling point of the reaction mixture, preferably from approximately -20°C to approximately $+150^\circ\text{C}$, and, if required, in a sealed vessel, under reduced, normal or elevated pressure, in an inert gas atmosphere and/or under anhydrous conditions. Especially advantageous reaction conditions can be seen from the examples.

Unless otherwise specified, the starting materials mentioned hereinabove and hereinbelow, which are used for the preparation of the compounds I or, where appropriate, the tautomers

thereof, in each case in free form or in salt form, are known or can be prepared by methods known per se, for example in accordance with the information given below.

Variant a)

The reactants can be reacted with each other as such, i. e. without addition of a solvent or diluent, for example in the melt. In most cases, however, it is advantageous to add an inert solvent or diluent or a mixture of these. Examples of such solvents or diluents which may be mentioned are: aromatic, aliphatic and alicyclic hydrocarbons and halohydrocarbons such as benzene, toluene, xylene, mesitylene, tetralin, chlorobenzene, dichlorobenzene, bromobenzene, petroleum ether, hexane, cyclohexane, dichloromethane, trichloromethane, tetrachloromethane, dichloroethane, trichloroethene or tetrachloroethene; esters such as ethyl acetate; ethers such as diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, tert-butyl methyl ether, ethyleneglycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol dimethyl ether, dimethoxydiethyl ether, tetrahydrofuran or dioxane; ketones, such as acetone, methyl ethyl ketone or methyl isobutyl ketone; alcohols, such as methanol, ethanol, propanol, isopropanol, butanol, ethylene glycol or glycerol; amides such as N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone or hexamethylphosphoric triamide; nitriles, such as acetonitrile or propionitrile; and sulfoxides, such as dimethyl sulfoxide.

The reaction is advantageously carried out in a temperature range from approximately -80°C to approximately $+140^{\circ}\text{C}$, preferably from approximately -30°C to approximately $+100^{\circ}\text{C}$, in many cases in the range between room temperature and approximately $+80^{\circ}\text{C}$.

Variant b)

Examples of suitable sulfurising agents are Lawesson's reagent and phosphorus pentasulfide.

The reactants can be reacted with each other as such, i.e. without adding a solvent or diluent. In most cases, however, it is advantageous to add an inert solvent or diluent or a mixture of these. Examples of suitable solvents or diluents are of the type described under variant a).

The reaction is advantageously carried out in a temperature range from approximately

-80°C to approximately +140°C, preferably from approximately -20°C to approximately +100°C, in many cases from approximately 0°C to approximately +80°C.

Variant c)

Examples of suitable leaving groups X_1 in the compounds IV are hydroxy, C_1 - C_8 alkoxy, halo- C_1 - C_8 alkoxy, C_1 - C_8 alkanoyloxy, mercapto, C_1 - C_8 alkylthio, halo- C_1 - C_8 alkylthio, C_1 - C_8 alkylsulfonyloxy, halo- C_1 - C_8 alkylsulfonyloxy, benzenesulfonyloxy, toluenesulfonyloxy and halogen, such as chlorine. Preferred are hydroxy, C_1 - C_8 alkoxy and chlorine.

The reactants can be reacted with each other as such, i.e. without adding a solvent or diluent. In most cases, however, it is advantageous to add an inert solvent or diluent or a mixture of these. Examples of suitable solvents or diluents are of the type described under variant a).

The reaction is advantageously carried out in a temperature range from approximately -80°C to approximately +140°C, preferably from approximately -20°C to approximately +100°C, in many cases in the range between room temperature and the reflux temperature of the reaction mixture.

Variant d)

Examples of suitable leaving groups X_2 in the compounds VI are hydroxy, C_1 - C_8 alkoxy, halo- C_1 - C_8 alkoxy, C_1 - C_8 alkanoyloxy, mercapto, C_1 - C_8 alkylthio, halo- C_1 - C_8 alkylthio, C_1 - C_8 alkylsulfonyloxy, halo- C_1 - C_8 alkylsulfonyloxy, benzenesulfonyloxy, toluenesulfonyloxy and halogen, such as chlorine. Preferred are hydroxy and chlorine.

The reactants can preferably be reacted in the presence of a base. Examples of suitable bases for facilitating the detachment of HX_2 are alkali metal or alkaline earth metal hydroxides, alkali metal or alkaline earth metal hydrides, alkali metal or alkaline earth metal amides, alkali metal or alkaline earth metal alkoxides, alkali metal or alkaline earth metal acetates, alkali metal or alkaline earth metal carbonates, alkali metal or alkaline earth metal dialkylamides or alkali metal or alkaline earth metal alkylsilylamides, alkylamines, alkylenediamines, free or N-alkylated saturated or unsaturated cycloalkylamines, basic heterocycles, ammonium hydroxides and carbocyclic amines. Examples which may be mentioned are sodium hydroxide, sodium hydride, sodium amide, sodium methoxide, sodium acetate, sodium carbonate, potassium tert-butoxide, potassium hydroxide, potassium carbonate, potassium

hydride, lithium diisopropylamide, potassium bis(trimethylsilyl)amide, calcium hydride, triethylamine, diisopropylethylamine, triethylenediamine, cyclohexylamine, N-cyclohexyl-N,N-dimethylamine, N,N-diethylaniline, pyridine, 4-(N,N-dimethylamino)pyridine, quinuclidine, N-methylmorpholine, benzyltrimethylammonium hydroxide and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

The reactants can be reacted with each other as such, i.e. without adding a solvent or diluent. In most cases, however, it is advantageous to add an inert solvent or diluent or a mixture of these. Examples of suitable solvents or diluents are of the type described under variant a). If the reaction is carried out in the presence of a base, bases which are employed in excess, such as triethylamine, pyridine, N-methylmorpholine or N,N-diethylaniline, may also act as solvents or diluents.

The reaction is advantageously carried out in a temperature range from approximately -80°C to approximately $+140^{\circ}\text{C}$, preferably from approximately -30°C to approximately $+100^{\circ}\text{C}$, in many cases in the range between room temperature and approximately $+80^{\circ}\text{C}$.

The compounds II, IV and V and, where appropriate, the tautomers thereof, in each case in free form or in salt form, are novel and are also subjects of the invention. Some of the compounds III and VI and, where appropriate, the tautomers thereof, in each case in free form or in salt form, are novel and are also subjects of the invention.

Further subjects of the invention are the processes for the preparation of the compounds of the formulae II, IV and V or, where appropriate, the tautomers thereof, in each case in free form or in salt form, and the processes for the preparation of the novel compounds of the formulae III and VI or, where appropriate, the tautomers thereof, in each case in free form or in salt form, which processes are carried out in a manner known per se.

A compound I can be converted in a manner known per se into another compound I by replacing one or more substituents of the starting compound I in the customary manner by (an)other substituent(s) according to the invention.

For example,

- in compounds I, in which R_2 is hydrogen, this hydrogen R_2 can be replaced by a substituent R_2 , which is different from hydrogen; or
- in compounds I, in which R_3 is hydrogen, this hydrogen R_3 can be replaced by a substituent R_3 , which is different from hydrogen.

Depending on the choice of the reaction conditions and starting materials which are suitable in each case, it is possible, for example, in one reaction step only to replace one substituent by another substituent according to the invention, or a plurality of substituents can be replaced by other substituents according to the invention in the same reaction step.

Salts of compounds I can be prepared in a manner known per se. Thus, for example, acid addition salts of compounds I are obtained by treatment with a suitable acid or a suitable ion exchanger reagent and salts with bases are obtained by treatment with a suitable base or with a suitable ion exchanger reagent.

Salts of compounds I can be converted in the customary manner into the free compounds I, acid addition salts, for example, by treatment with a suitable basic compound or with a suitable ion exchanger reagent and salts with bases, for example, by treatment with a suitable acid or with a suitable ion exchanger reagent.

Salts of compounds I can be converted in a manner known per se into other salts of compounds I, acid addition salts, for example, into other acid addition salts, for example by treatment of a salt of inorganic acid such as hydrochloride with a suitable metal salt such as a sodium, barium or silver salt, of an acid, for example with silver acetate, in a suitable solvent in which an inorganic salt which forms, for example silver chloride, is insoluble and thus precipitates from the reaction mixture.

Depending on the procedure or the reaction conditions, the compounds I, which have salt-forming properties can be obtained in free form or in the form of salts.

The compounds I and, where appropriate, the tautomers thereof, in each case in free form or in salt form, can be present in the form of one of the isomers which are possible or as a mixture of these, for example in the form of pure isomers, such as antipodes and/or diastereomers, or as isomer mixtures, such as enantiomer mixtures, for example racemates,

diastereomer mixtures or racemate mixtures, depending on the number, absolute and relative configuration of asymmetric carbon atoms which occur in the molecule and/or depending on the configuration of non-aromatic double bonds which occur in the molecule; the invention relates to the pure isomers and also to all isomer mixtures which are possible and is to be understood in each case in this sense hereinabove and hereinbelow, even when stereochemical details are not mentioned specifically in each case.

Diastereomer mixtures or racemate mixtures of compounds I, in free form or in salt form, which can be obtained depending on which starting materials and procedures have been chosen can be separated in a known manner into the pure diastereomers or racemates on the basis of the physicochemical differences of the components, for example by fractional crystallization, distillation and/or chromatography.

Enantiomer mixtures, such as racemates, which can be obtained in a similar manner can be resolved into the optical antipodes by known methods, for example by recrystallization from an optically active solvent, by chromatography on chiral adsorbents, for example high-performance liquid chromatography (HPLC) on acetyl cellulose, with the aid of suitable microorganisms, by cleavage with specific, immobilized enzymes, via the formation of inclusion compounds, for example using chiral crown ethers, where only one enantiomer is complexed, or by conversion into diastereomeric salts, for example by reacting a basic end-product racemate with an optically active acid, such as a carboxylic acid, for example camphor, tartaric or malic acid, or sulfonic acid, for example camphorsulfonic acid, and separating the diastereomer mixture which can be obtained in this manner, for example by fractional crystallization based on their differing solubilities, to give the diastereomers, from which the desired enantiomer can be set free by the action of suitable agents, for example basic agents.

Pure diastereomers or enantiomers can be obtained according to the invention not only by separating suitable isomer mixtures, but also by generally known methods of diastereoselective or enantioselective synthesis, for example by carrying out the process according to the invention with starting materials of a suitable stereochemistry.

It is advantageous to isolate or synthesize in each case the biologically more effective isomer, for example enantiomer or diastereomer, or isomer mixture, for example enantiomer mixture or diastereomer mixture, if the individual components have a different biological activity.

The compounds I and, where appropriate, the tautomers thereof, in each case in free form or in salt form, can, if appropriate, also be obtained in the form of hydrates and/or include other solvents, for example those which may have been used for the crystallization of compounds which are present in solid form.

The invention relates to all those embodiments of the process by which, starting from a compound obtainable at any level of the process as starting material or intermediate, all or some of the missing steps are carried out or a starting material is used in the form of a derivative and/or salt and/or racemates or antipodes thereof or, in particular, is formed under the reaction conditions.

Those starting materials and intermediates, in each case in free form or in salt form, which lead to the compounds I or salts thereof which have been described at the outset as being particularly valuable are preferably used in the process of the present invention.

In particular, the invention relates to the preparation processes described in the Examples P1 to P11.

Starting materials and intermediates, in each case in free form or salt form, which are used in accordance with the invention for the preparation of the compounds I or salts thereof and which are novel, a process for their preparation, and their use as starting materials and intermediates for the preparation of the compounds I are also a subject of the invention; in particular, this applies to the compounds II, IV and V.

The compounds I according to the invention are preventively and/or curatively valuable active ingredients in the field of pest control, even at low rates of application, which have a very favorable biocidal spectrum and are well tolerated by warm-blooded species, fish and plants. The active ingredients according to the invention act against all or individual developmental stages of normally sensitive, but also resistant, animal pests, such as insects or representatives of the order Acarina. The insecticidal or acaricidal activity of the active ingredients according to the invention can manifest itself directly, i. e. in destruction of the pests, which takes place either immediately or only after some time has elapsed, for example

during ecdysis, or indirectly, for example in a reduced oviposition and/or hatching rate, a good activity corresponding to a destruction rate (mortality) of at least 50 to 60%.

Examples of the abovementioned animal pests are:

from the order *Acarina*, for example,

Acarus siro, *Aceria sheldoni*, *Aculus schlechtendali*, *Amblyomma* spp., *Argas* spp., *Boophilus* spp., *Brevipalpus* spp., *Bryobia praetiosa*, *Calipitimerus* spp., *Chorioptes* spp., *Derma-nyssus gallinae*, *Eotetranychus carpini*, *Eriophyes* spp., *Hyalomma* spp., *Ixodes* spp., *Olygonychus pratensis*, *Ornithodoros* spp., *Panonychus* spp., *Phyllocoptruta oleivora*, *Polyphagotarsonemus latus*, *Psoroptes* spp., *Rhipicephalus* spp., *Rhizoglyphus* spp., *Sarcoptes* spp., *Tarsonemus* spp. and *Tetranychus* spp.;

from the order *Anoplura*, for example,

Haematopinus spp., *Linognathus* spp., *Pediculus* spp., *Pemphigus* spp. and *Phylloxera* spp.;

from the order *Coleoptera*, for example,

Agriotes spp., *Anthonomus* spp., *Atomaria linearis*, *Chaetocnema tibialis*, *Cosmopolites* spp., *Curculio* spp., *Dermestes* spp., *Diabrotica* spp., *Epilachna* spp., *Eremnus* spp., *Leptinotarsa decemlineata*, *Lissorhoptrus* spp., *Melolontha* spp., *Orycaephilus* spp., *Otiorynchus* spp., *Phlyctinus* spp., *Popillia* spp., *Psylliodes* spp., *Rhizopertha* spp., *Scarabeidae*, *Sitophilus* spp., *Sitotroga* spp., *Tenebrio* spp., *Tribolium* spp. and *Trogoderma* spp.;

from the order *Diptera*, for example,

Aedes spp., *Antherigona soccata*, *Bibio hortulanus*, *Calliphora erythrocephala*, *Ceratitis* spp., *Chrysomya* spp., *Culex* spp., *Cuterebra* spp., *Dacus* spp., *Drosophila melanogaster*, *Fannia* spp., *Gastrophilus* spp., *Glossina* spp., *Hypoderma* spp., *Hyppobosca* spp., *Liriomyza* spp., *Lucilia* spp., *Melanagromyza* spp., *Musca* spp., *Oestrus* spp., *Orseolia* spp., *Oscinella frit*, *Pegomyia hyoscyami*, *Phorbia* spp., *Rhagoletis pomonella*, *Sciara* spp., *Stomoxys* spp., *Tabanus* spp., *Tannia* spp. and *Tipula* spp.;

from the order *Heteroptera*, for example,

Cimex spp., *Distantiella theobroma*, *Dysdercus* spp., *Euchistus* spp., *Eurygaster* spp., *Lep-tocoris* spp., *Nezara* spp., *Piesma* spp., *Rhodnius* spp., *Sahlbergella singularis*, *Scotinophara* spp. and *Triatoma* spp.;

from the order *Homoptera*, for example,

Aleurothrixus floccosus, *Aleyrodes brassicae*, *Aonidiella* spp., *Aphididae*, *Aphis* spp., *Aspidiotus* spp., *Bemisia tabaci*, *Ceroplaster* spp., *Chrysomphalus aonidium*, *Chrysomphalus dictyospermi*, *Coccus hesperidum*, *Empoasca* spp., *Eriosoma larigerum*, *Erythroneura* spp.,

Gascardia spp., Laodelphax spp., Lecanium corni, Lepidosaphes spp., Macrosiphus spp., Myzus spp., Nephrotettix spp., Nilaparvata spp., Parlatoria spp., Pemphigus spp., Planococcus spp., Pseudaulacaspis spp., Pseudococcus spp., Psylla spp., Pulvinaria aethiopica, Quadraspidiotus spp., Rhopalosiphum spp., Saissetia spp., Scaphoideus spp., Schizaphis spp., Sitobion spp., Trialeurodes vaporariorum, Trioza erytrae and Unaspis citri;

from the order *Hymenoptera*, for example,

Acromyrmex, Atta spp., Cephus spp., Diprion spp., Diprionidae, Gilpinia polytoma, Hoplocampa spp., Lasius spp., Monomorium pharaonis, Neodiprion spp., Solenopsis spp. and Vespa spp.;

from the order *Isoptera*, for example,

Reticulitermes spp.;

from the order *Lepidoptera*, for example,

Acleris spp., Adoxophyes spp., Aegeria spp., Agrotis spp., Alabama argillaceae, Amylois spp., Anticarsia gemmatilis, Archips spp., Argyrotaenia spp., Autographa spp., Busseola fusca, Cadra cautella, Carposina nipponensis, Chilo spp., Choristoneura spp., Clysia ambiguella, Cnaphalocrocis spp., Cnephasia spp., Cochylis spp., Coleophora spp., Crocidolomia binotalis, Cryptophlebia leucotreta, Cydia spp., Diatraea spp., Diparopsis castanea, Earias spp., Ephestia spp., Eucosma spp., Eupoecilia ambiguella, Euproctis spp., Euxoa spp., Grapholita spp., Hedya nubiferana, Heliothis spp., Hellula undalis, Hyphantria cunea, Keiferia lycopersicella, Leucoptera scitella, Lithocollethis spp., Lobesia botrana, Lymantria spp., Lyonetia spp., Malacosoma spp., Mamestra brassicae, Manduca sexta, Operophtera spp., Ostrinia nubilalis, Pammene spp., Pandemis spp., Panolis flammea, Pectinophora gossypiella, Phthorimaea operculella, Pieris rapae, Pieris spp., Plutella xylostella, Prays spp., Scirpophaga spp., Sesamia spp., Sparganothis spp., Spodoptera spp., Synanthedon spp., Thaumetopoea spp., Tortrix spp., Trichoplusia ni and Yponomeuta spp.;

from the order *Mallophaga*, for example,

Damalinea spp. and Trichodectes spp.;

from the order *Orthoptera*, for example,

Blatta spp., Blattella spp., Gryllotalpa spp., Leucophaea maderae, Locusta spp., Periplaneta spp. and Schistocerca spp.;

from the order *Psocoptera*, for example,

Liposcelis spp.;

from the order *Siphonaptera*, for example,

Ceratophyllus spp., Ctenocephalides spp. and Xenopsylla cheopis;

from the order *Thysanoptera*, for example,

Frankliniella spp., Hercinothrips spp., Scirtothrips aurantii, Taeniothrips spp., Thrips palmi and Thrips tabaci; and

from the order *Thysanura*, for example,

Lepisma saccharina.

The active ingredients according to the invention can be used for controlling, i. e. containing or destroying, pests of the abovementioned type which occur in particular on plants, especially on useful plants and ornamentals in agriculture, in horticulture and in forests, or on organs, such as fruits, flowers, foliage, stalks, tubers or roots, of such plants, and in some cases even plant organs which are formed at a later point in time remain protected against these pests.

Suitable target crops are, in particular, cereals, such as wheat, barley, rye, oats, rice, maize or sorghum; beet, such as sugar or fodder beet; fruit, for example pomaceous fruit, stone fruit or soft fruit, such as apples, pears, plums, peaches, almonds, cherries or berries, for example strawberries, raspberries or blackberries; leguminous crops, such as beans, lentils, peas or soya; oil crops, such as oilseed rape, mustard, poppies, olives, sunflowers, coconut, castor, cocoa or ground nuts; cucurbits, such as pumpkins, cucumbers or melons; fibre plants, such as cotton, flax, hemp or jute; citrus fruit, such as oranges, lemons, grapefruit or tangerines; vegetables, such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes or bell peppers; Lauraceae, such as avocado, Cinnamomum or camphor; and also tobacco, nuts, coffee, eggplants, sugarcane, tea, pepper, grapevines, hops, the plantain family, latex plants and ornamentals.

The active ingredients according to the invention are especially suitable for controlling Aphis craccivora, Diabrotica balteata, Heliothis virescens, Myzus persicae, Plutella xylostella and Spodoptera littoralis in cotton, vegetable, maize, rice and soya crops.

Other fields of application of the active ingredients according to the invention are the protection of stored products and stores and of material, such as wood, textiles, floor coverings or buildings, and, in the hygiene sector, particularly the protection of humans, domestic animals and productive livestock against pests of the abovementioned type.

The invention therefore also relates to pesticidal compositions such as emulsifiable concentrates, suspension concentrates, directly sprayable or dilutable solutions, spreadable pastes, dilute emulsions, soluble powders, dispersible powders, wettable powders, dusts, granules or encapsulations in polymeric substances, which comprise - at least - one of the active ingredients according to the invention and which are to be selected to suit the intended aims and the prevailing circumstances.

In these compositions, the active ingredient is employed in pure form, a solid active ingredient for example in a specific particle size, or, preferably, together with - at least - one of the auxiliaries conventionally used in the art of formulation, such as extenders, for example solvents or solid carriers, or such as surface-active compounds (surfactants).

Examples of suitable solvents are: unhydrogenated or partially hydrogenated aromatic hydrocarbons, preferably the fractions C₈ to C₁₂ of alkylbenzenes, such as xylene mixtures, alkylated naphthalenes or tetrahydronaphthalene, aliphatic or cycloaliphatic hydrocarbons, such as paraffins or cyclohexane, alcohols such as ethanol, propanol or butanol, glycols and their ethers and esters such as propylene glycol, dipropylene glycol ether, ethylene glycol or ethylene glycol monomethyl ether or ethylene glycol monoethyl ether, ketones, such as cyclohexanone, isophorone or diacetone alcohol, strongly polar solvents, such as N-methylpyrrolid-2-one, dimethyl sulfoxide or N,N-dimethylformamide, water, unepoxidized or epoxidized vegetable oils, such as unepoxidized or epoxidized rapeseed, castor, coconut or soya oil, and silicone oils.

Solid carriers which are used for example for dusts and dispersible powders are, as a rule, ground natural minerals such as calcite, talc, kaolin, montmorillonite or attapulgite. To improve the physical properties, it is also possible to add highly disperse silicas or highly disperse absorptive polymers. Suitable particulate adsorptive carriers for granules are porous types, such as pumice, brick grit, sepiolite or bentonite, and suitable non-sorptive carrier materials are calcite or sand. In addition, a large number of granulated materials of inorganic or organic nature can be used, in particular dolomite or comminuted plant residues.

Suitable surface-active compounds are, depending on the type of the active ingredient to be formulated, non-ionic, cationic and/or anionic surfactants or surfactant mixtures which have good emulsifying, dispersing and wetting properties. The surfactants mentioned below are

only to be considered as examples; a large number of further surfactants which are conventionally used in the art of formulation and suitable according to the invention are described in the relevant literature.

Suitable non-ionic surfactants are, especially, polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, of saturated or unsaturated fatty acids or of alkyl phenols which may contain approximately 3 to approximately 30 glycol ether groups and approximately 8 to approximately 20 carbon atoms in the (cyclo)aliphatic hydrocarbon radical or approximately 6 to approximately 18 carbon atoms in the alkyl moiety of the alkyl phenols. Also suitable are water-soluble polyethylene oxide adducts with polypropylene glycol, ethylenediaminopolypropylene glycol or alkyl polypropylene glycol having 1 to approximately 10 carbon atoms in the alkyl chain and approximately 20 to approximately 250 ethylene glycol ether groups and approximately 10 to approximately 100 propylene glycol ether groups. Normally, the abovementioned compounds contain 1 to approximately 5 ethylene glycol units per propylene glycol unit. Examples which may be mentioned are nonylphenoxypolyethoxyethanol, castor oil polyglycol ether, polypropylene glycol/polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol or octylphenoxypolyethoxyethanol. Also suitable are fatty acid esters of polyoxyethylene sorbitan, such as polyoxyethylene sorbitan trioleate.

The cationic surfactants are, especially, quarternary ammonium salts which generally have at least one alkyl radical of approximately 8 to approximately 22 C atoms as substituents and as further substituents (unhalogenated or halogenated) lower alkyl or hydroxyalkyl or benzyl radicals. The salts are preferably in the form of halides, methylsulfates or ethylsulfates. Examples are stearyltrimethylammonium chloride and benzylbis(2-chloroethyl)ethylammonium bromide.

Examples of suitable anionic surfactants are water-soluble soaps or water-soluble synthetic surface-active compounds. Examples of suitable soaps are the alkali, alkaline earth or (unsubstituted or substituted) ammonium salts of fatty acids having approximately 10 to approximately 22 C atoms, such as the sodium or potassium salts of oleic or stearic acid, or of natural fatty acid mixtures which are obtainable for example from coconut or tall oil; mention must also be made of the fatty acid methyl taurates. However, synthetic surfactants are used more frequently, in particular fatty sulfonates, fatty sulfates, sulfonated benzimidazole derivatives or alkylaryl sulfonates. As a rule, the fatty sulfonates and fatty sulfates are present

as alkali, alkaline earth or (substituted or unsubstituted) ammonium salts and they generally have an alkyl radical of approximately 8 to approximately 22 C atoms, alkyl also to be understood as including the alkyl moiety of acyl radicals; examples which may be mentioned are the sodium or calcium salts of lignosulfonic acid, of the dodecylsulfuric ester or of a fatty alcohol sulfate mixture prepared from natural fatty acids. This group also includes the salts of the sulfuric esters and sulfonic acids of fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonyl groups and a fatty acid radical of approximately 8 to approximately 22 C atoms. Examples of alkylarylsulfonates are the sodium, calcium or triethanolammonium salts of decylbenzenesulfonic acid, of dibutyl-naphthalenesulfonic acid or of a naphthalenesulfonic acid/formaldehyde condensate. Also possible are, furthermore, suitable phosphates, such as salts of the phosphoric ester of a p-nonylphenol/(4-14)ethylene oxide adduct, or phospholipids.

As a rule, the compositions comprise from 0.0001 to 99.9999 %, in particular 0.1 to 95 %, of active ingredient, and 0.0001 to 99.9999 %, in particular 5 to 99.9 %, of - at least - one solid or liquid auxiliary, it being possible, as a rule, for 0 to 25 %, in particular 0.1 to 20 %, of the compositions to be surfactants (% in each case is per cent by weight). While concentrated compositions are more preferred as commercially available goods, the end user uses, as a rule, dilute compositions which have considerably lower concentrations of active ingredient.

The activity of the compositions according to the invention can be broadened considerably, and adapted to prevailing circumstances, by adding other insecticidally or acaricidally active ingredients. Suitable additions to active ingredients here are, for example, representatives of the following classes of active ingredients: organophosphorus compounds, nitrophenol derivatives, thioureas, juvenile hormones, formamidines, benzophenone derivatives, ureas, pyrrole derivatives, carbamates, pyrethroids, chlorinated hydrocarbons, acylureas, pyridyl-methyleneamino derivatives, macrolides, neonicotinoids and *Bacillus thuringiensis* preparations. Examples of especially suitable mixing partners include: azamethiphos; chlorfenvinphos; cypermethrin, cypermethrin high-cis; cyromazine; diafenthiuron; diazinon; dichlorvos; dicrotophos; dicyclanil; fenoxycarb; fluazuron; furathiocarb; isazofos; iodfenphos; kinoprene; lufenuron; methacriphos; methidathion; monocrotophos; phosphamidon; profenofos; diofenolan; a compound obtainable from the *Bacillus thuringiensis* strain GC91 or from strain NCTC11821; pymetrozine; bromopropylate; methoprene; disulfoton; quinalphos; tau-fluvalinate; thiocyclam; thiometon; aldicarb; azinphos-methyl; benfuracarb; bifenthrin;

buprofezin; carbofuran; dibutylaminothio; cartap; chlorfluazuron; chlorpyrifos; cyfluthrin; lambda-cyhalothrin; alpha-cypermethrin; zeta-cypermethrin; deltamethrin; diflubenzuron; endosulfan; ethiofencarb; fenitrothion; fenobucarb; fenvalerate; formothion; methiocarb; heptenophos; imidacloprid; thiamethoxam; clothianidin; isoprocarb; methamidophos; methomyl; mevinphos; parathion; parathion-methyl; phosalone; pirimicarb; propoxur; teflubenzuron; terbufos; triazamate; fenobucarb; tebufenozide; fipronil; beta-cyfluthrin; silafluofen; fenpyroximate; pyridaben; fenazaquin; pyriproxyfen; pyrimidifen; nitenpyram; acetamiprid; emamectin; emamectin-benzoate; spinosad; a plant extract that is active against insects; a preparation that comprises nematodes and is active against insects; a preparation obtainable from *Bacillus subtilis*; a preparation that comprises fungi and is active against insects; a preparation that comprises viruses and is active against insects; chlorfenapyr; acephate; acrinathrin; alanycarb; alphamethrin; amitraz; AZ 60541; azinphos A; azinphos M; azocyclotin; bendiocarb; bensultap; beta-cyfluthrin; BPMC; brofenprox; bromophos A; bufencarb; buto-carboxin; butylpyridaben; cadusafos; carbaryl; carbophenothion; chloethocarb; chlorethoxyfos; chlormephos; cis-resmethrin; clocythrin; clofentezine; cyanophos; cycloprothrin; cyhexatin; demeton M; demeton S; demeton-S-methyl; dichlofenthion; dicliphos; diethion; dimethoate; dimethylvinphos; dioxathion; edifenphos; esfenvalerate; ethion; ethofenprox; ethoprophos; etrimphos; fenamiphos; fenbutatin oxide; fenothiocarb; fenpropathrin; fenpyrad; fenthion; fluazinam; flucycloxuron; flucythrinate; flufenoxuron; flufenprox; fonophos; fosthiazate; fubfenprox; HCH; hexaflumuron; hexythiazox; IKI-220; iprobenfos; isofenphos; isoxathion; ivermectin; malathion; mecarbarn; mesulfenphos; metaldehyde; metolcarb; milbemectin; moxidectin; naled; NC 184; omethoate; oxamyl; oxydemethon M; oxydeprofos; permethrin; phenthoate; phorate; phosmet; phoxim; pirimiphos M; pirimiphos E; promecarb; propaphos; prothiofos; prothoate; pyrachlophos; pyradaphenthion; pyresmethrin; pyrethrum; tebufenozide; salithion; sebufos; sulfotep; sulprofos; tebufenpyrad; tebupirimphos; tefluthrin; temephos; terbam; tetrachlorvinphos; thiadiazin; thiafenox; thiodicarb; thiofanox; thionazin; thuringiensin; tralomethrin; triarathene; triazophos; triazuron; trichlorfon; triflumuron; trimethacarb; vamidothion; xylylcarb; YI 5301/5302; zetamethrin; DPX-MP062 — indoxacarb; methoxyfenozide; bifentazate; XMC (3,5-xylyl methylcarbamate); or the fungus pathogen *Metarhizium anisopliae*.

The compositions can also comprise further solid or liquid auxiliaries, such as stabilizers, for example unepoxidized or epoxidized vegetable oils (for example epoxidized coconut oil, rapeseed oil or soya oil), antifoams, for example silicone oil, preservatives, viscosity

regulators, binders and/or tackifiers, fertilizers or other active ingredients for achieving specific effects, for example bactericides, fungicides, nematocides, plant activators, molluscicides or herbicides.

The compositions according to the invention are prepared in a manner known per se, in the absence of auxiliaries for example by grinding, screening and/or compressing a solid active ingredient and in the presence of at least one auxiliary for example by intimately mixing and/or grinding the active ingredient with the auxiliary (auxiliaries). These processes for the preparation of the compositions and the use of the compounds I for the preparation of these compositions are also a subject of the invention.

The application methods for the compositions, that is the methods of controlling pests of the abovementioned type, such as spraying, atomizing, dusting, brushing on, dressing, scattering or pouring - which are to be selected to suit the intended aims of the prevailing circumstances - and the use of the compositions for controlling pests of the abovementioned type are other subjects of the invention. Typical rates of concentration are between 0.1 and 1000 ppm, preferably between 0.1 and 500 ppm, of active ingredient. The rate of application per hectare is generally 1 to 2000 g of active ingredient per hectare, in particular 10 to 1000 g/ha, preferably 10 to 600 g/ha.

A preferred method of application in the field of crop protection is application to the foliage of the plants (foliar application), it being possible to select frequency and rate of application to match the danger of infestation with the pest in question. Alternatively, the active ingredient can reach the plants via the root system (systemic action), by drenching the locus of the plants with a liquid composition or by incorporating the active ingredient in solid form into the locus of the plants, for example into the soil, for example in the form of granules (soil application). In the case of paddy rice crops, such granules can be metered into the flooded paddy-field.

The compositions according to the invention are also suitable for the protection of plant propagation material, for example seeds, such as fruit, tubers or kernels, or nursery plants, against pests of the abovementioned type. The propagation material can be treated with the compositions prior to planting, for example seed can be treated prior to sowing. Alternatively, the compositions can be applied to seed kernels (coating), either by soaking the kernels in a

liquid composition or by applying a layer of a solid composition. It is also possible to apply the compositions when the propagation material is planted to the site of application, for example into the seed furrow during drilling. These treatment methods for plant propagation material and the plant propagation material thus treated are further subjects of the invention.

The examples which follow are intended to illustrate the invention. They do not limit the invention. Temperatures are given in degrees Celsius.

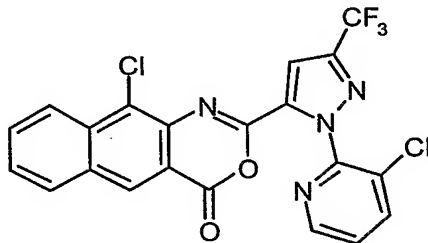
Preparation Examples

Example P1



1.9 g (14.7 mmol) of N-chlorosuccinimide and 10 mg of 2,2'-azoisobutyric nitrile are added to a suspension of 2.5 g (13.3 mmol) of 2-amino-3-carboxy-naphthalene in 100 ml of tetrachloromethane. The reaction mixture is stirred for 18 hours at room temperature, treated with 250 ml of aqueous sodium chloride solution and extracted with ethyl acetate (3 x 250 ml). The combined organic layers are dried over magnesium sulfate and filtered, and the filtrate is concentrated in vacuo. This gives the title compound in the form of a brown solid [¹H-NMR (CDCl₃): 8.53 (s, 1H), 7.98 (d, 1H), 7.73 (d, 1H), 7.55 (t, 1H), 7.25 (t, 1H)].

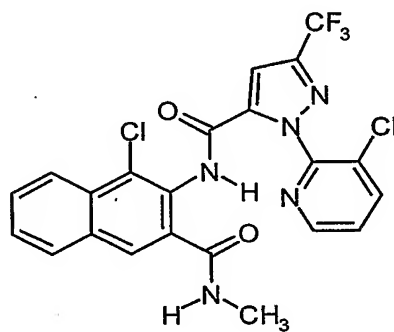
Example P2



In a nitrogen atmosphere 0.5 ml (5.75 mmol) of oxalyl chloride are added dropwise at room temperature with stirring to a suspension of 295 mg (1.0 mmol) of 5-carboxy-1-(3-chloropyrid-2-yl)-3-trifluoromethyl-pyrazole in 2 ml of dichloromethane. The reaction mixture is stirred for 1 hour and then added dropwise to a solution of 0.25 g (1 mmol) of the title compound of

Example P1 in a mixture of 20 ml of dichloromethane and 0.38 ml of triethylamine. The reaction mixture is subsequently stirred for 3 hours. Further 0.7 ml of triethylamine are added, followed by the addition of a single portion of 0.22 ml (2.8 mmol) of methane sulfonic acid chloride. The reaction mixture is then stirred for 18 hours and concentrated in vacuo, and the residue is purified by column chromatography [silica gel; hexane/ethyl acetate (3:1)], which gives the title compound [$^1\text{H-NMR}$ (CDCl_3): 8.78 (s, 1H), 8.61 (m, 1H), 8.30 (m, 2H), 8.03 (dd, 1H), 7.78 (m, 1H), 7.67 (m, 1H), 7.56 (m, 2H); MS (electrospray): 477, 479, 481 ((M+H) $^+$)].

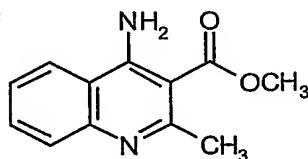
Example P3



(T1.1)

In a nitrogen atmosphere 1 ml of a solution (2.0 M) of methylamine in anhydrous tetrahydrofuran is added with stirring to a solution of 0.07 g (0.15 mmol) of the title compound of Example P2 in 5 ml of anhydrous tetrahydrofuran. The reaction mixture is heated to 50° for 1 hour, allowed to cool to room temperature and concentrated in vacuo, and the residue is purified by column chromatography [silica gel; hexane, followed by hexane/ethyl acetate (3:1)], which gives the title compound T1.1 [$^1\text{H-NMR}$ (DMSO-d_6): 10.80 (s, 1H), 8.53 (d, 1H), 8.45 (br s, 1H), 8.21 (m, 2H), 8.08 (m, 2H), 7.87 (s, 1H), 7.78 (t, 1H), 7.70 (t, 1H), 7.64 (dd, 1H), 2.70 (d, 3H); MS (electrospray): 508, 510, 512 ((M+H) $^+$)].

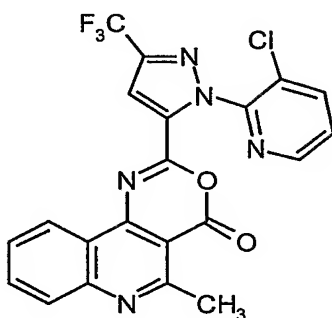
Example P4



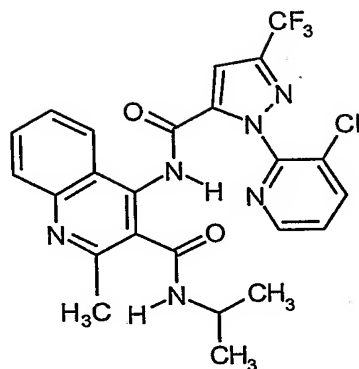
0.91 ml (8.46 mmol) of methyl acetoacetate and 1.98 ml (16.9 mmol) of tin tetrachloride are added to a solution of 1 g (8.46 mmol) of 1-amino-2-cyano-benzene in 20 ml of toluene. The reaction mixture is heated to reflux for 2 hours, allowed to cool to room temperature and concentrated in vacuo. The residue is suspended in 250 ml of aqueous sodium carbonate

solution, and the suspension is stirred for 30 minutes, allowed to stand overnight and then extracted with ethyl acetate (3 x 250 ml). The combined organic layers are dried over magnesium sulfate and filtered, the filtrate is concentrated in vacuo, and the yellow solid residue is triturated with diethyl ether. This gives the title compound in the form of a yellow powder [$^1\text{H-NMR}$ (CDCl_3): 7.88 (d, 1H), 7.77 (d, 1H), 7.68 (m, 1H), 7.43 (m, 1H), 7.06 (br s, 2H), 3.96 (s, 3H), 2.82 (s, 3H); MS (electrospray): 217 ((M+H) $^+$)].

Example P5

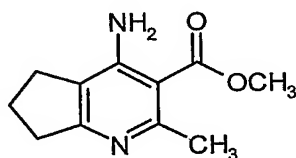


In a nitrogen atmosphere 4 drops of N,N-dimethylformamide and then 0.08 ml (0.93 mmol) of oxalyl chloride are added dropwise at room temperature with stirring to a suspension of 250 mg (0.86 mmol) of 5-carboxy-1-(3-chloropyrid-2-yl)-3-trifluoromethyl-pyrazole in 10 ml of dichloromethane. The reaction mixture is stirred for 1 hour, the solvent is removed in vacuo, and the residue is co-evaporated three times with toluene and then suspended in 3 ml of toluene to give the suspension "A". 105 mg (0.858 mmol) of 4-dimethylaminopyridine are added to a suspension of 185 mg (0.858 mmol) of the title compound of Example P4 in 3 ml of toluene to give the suspension "B". The suspension "A" is added to the suspension "B", for a complete transfer of the suspension "A" into the reaction flask the vessel containing the suspension "A" being rinsed out with a small amount of a mixture of toluene and a few drops of N,N-dimethylformamide. The reaction mixture is heated to reflux for 3 hours and then allowed to cool to room temperature. The yellow precipitate is filtered off and washed with diethyl ether. The filtrate is washed with 10 ml of water, and the water is back-extracted with ethyl acetate (2 x 50 ml). The combined organic layers are dried over magnesium sulfate and filtered, the filtrate is concentrated in vacuo, and the residue is purified by column chromatography [silica gel; hexane/ethyl acetate (1:2)], which gives the title compound [$^1\text{H-NMR}$ (CDCl_3): 8.66 (d, 1H), 8.09 (d, 1H), 8.03 (d, 1H), 7.86 (t, 1H), 7.67 (s, 1H), 7.67 (d, 1H), 7.45 (m, 1H), 7.40 (dd, 1H), 3.09 (s, 3H); MS (electrospray): 458 ((M+H) $^+$)].

Example P6

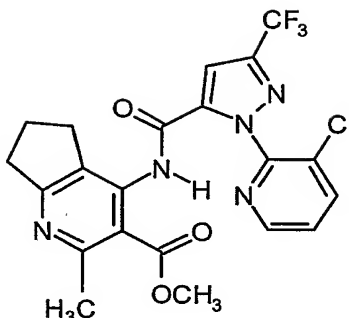
(T38.3)

0.022 ml (0.262 mmol) of isopropylamine are added with stirring to a suspension of 40 mg (0.087 mmol) of the title compound of Example P5 in 1 ml of anhydrous tetrahydrofuran. The reaction mixture is heated to 60° for 90 minutes, allowed to cool to room temperature and concentrated in vacuo, and the residue is purified by column chromatography [silica gel; methanol/dichloromethane (1:9)], which gives the title compound T38.3 [¹H-NMR (CDCl₃): 11.17 (s, 1H), 8.42 (d, 1H), 8.09 (s, 1H), 7.81 (d, 1H), 7.71 (t, 1H), 7.70 (d, 1H), 7.60 (d, 1H), 7.48 (t, 1H), 7.36 (m, 1H), 6.31 (d, 1H), 4.23 (m, 1H), 2.30 (s, 3H), 1.16 (d, 6H); MS (electrospray): 517 ((M+H)⁺)].

Example P7

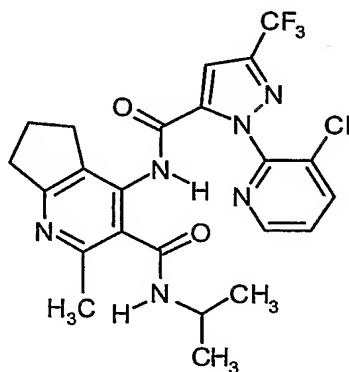
Starting from 1-amino-2-cyano-cyclopent-1-ene, the title compound can be prepared in a manner analogous to the procedure described in Example P4 [¹H-NMR (CDCl₃): 5.77 (br s, 2H), 3.90 (s, 3H), 2.97 (m, 2H), 2.70 (m, 2H), 2.15 (m, 2H); MS (electrospray): 207 ((M+H)⁺)].

Example P8



In a nitrogen atmosphere 4 drops of N,N-dimethylformamide and then 0.16 ml (1.86 mmol) of oxalyl chloride are added dropwise at room temperature with stirring to a suspension of 0.5 g (1.72 mmol) of 5-carboxy-1-(3-chloropyrid-2-yl)-3-trifluoromethyl-pyrazole in 20 ml of dichloromethane. The reaction mixture is stirred for 90 minutes, the solvent is removed in vacuo, and the residue is co-evaporated three times with toluene and then dissolved in 10 ml of tetrahydrofuran to give the solution "A". 0.24 ml (1.72 mmol) of triethylamine are added to a suspension of 195 mg (0.95 mmol) of the title compound of Example P7 in 10 ml of tetrahydrofuran to give the suspension "B". 5 ml of the solution "A" are added in portions over a period of 30 minutes to the suspension "B". The reaction mixture is stirred for 2.5 hours, treated with 10 ml of aqueous sodium hydrogen carbonate solution and extracted with ethyl acetate (2 x 40 ml). The combined organic layers are dried over magnesium sulfate and filtered, the filtrate is concentrated in vacuo, and the residue is purified by column chromatography (silica gel; ethyl acetate), which gives the title compound [$^1\text{H-NMR}$ (CDCl_3): 10.15 (s, 1H), 8.49 (d, 1H), 7.92 (d, 1H), 7.45 (m, 1H), 7.22 (s, 1H), 3.96 (s, 3H), 2.99 (m, 2H), 2.75 (m, 2H), 2.67 (s, 3H), 2.06 (m, 2H); MS (electrospray): 480 ((M+H) $^+$)].

Example P9



(T37.3)

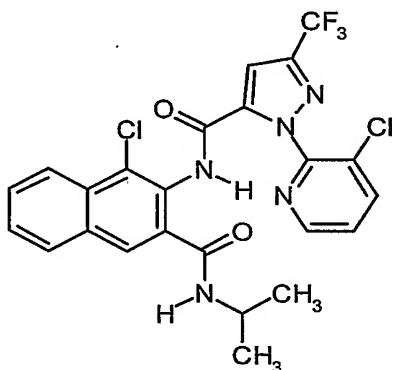
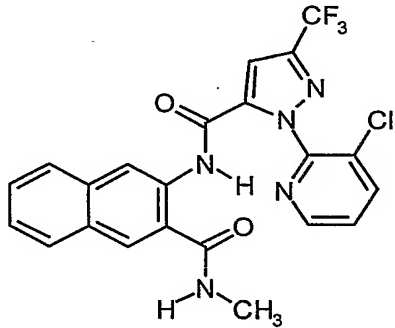
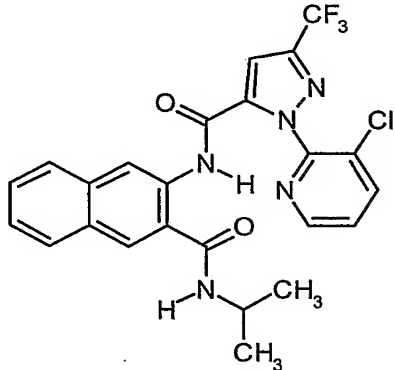
0.04 ml (0.47 mmol) of isopropylamine are added at room temperature with stirring to a mixture of 0.24 ml of a solution (2.0 M) of trimethylaluminium in hexane and 3 ml of

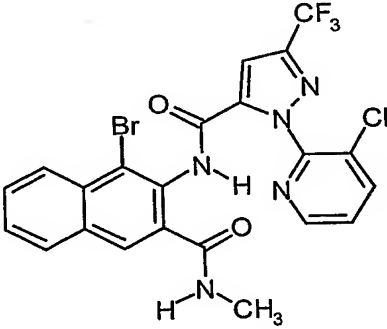
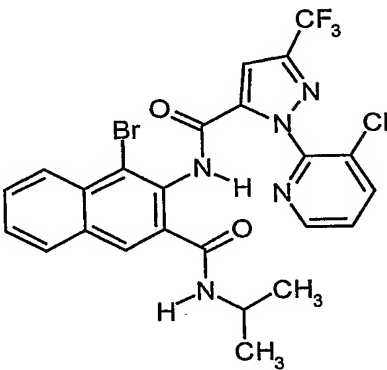
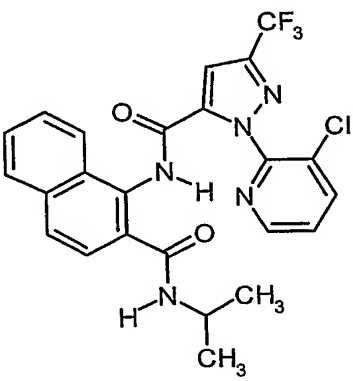
dichloromethane. The reaction mixture is stirred for 40 minutes. A solution of 110 mg (0.22 mmol) of the title compound of Example P8 in 3 ml of dichloromethane is added, and the reaction mixture is heated to reflux for 6 hours, allowed to cool to room temperature and to stand overnight and then poured into 20 ml of water. The mixture is extracted with dichloromethane (2 x 30 ml). The combined organic layers are dried over magnesium sulfate and filtered, the filtrate is concentrated in vacuo, and the residue is purified by column chromatography [silica gel; ethyl acetate/hexane (2:1), followed by neat ethyl acetate], which gives the title compound T37.3 [$^1\text{H-NMR}$ (CDCl_3): 10.69 (s, 1H), 8.49 (d, 1H), 7.88 (d, 1H), 7.70 (s, 1H), 7.42 (m, 1H), 5.89 (d, 1H), 4.24 (m, 1H), 2.87 (t, 2H), 2.57 (t, 2H), 2.49 (s, 3H), 2.02 (m, 2H), 1.19 (d, 6H); MS (electrospray): 507 ((M+H) $^+$)].

Example P10

The compounds listed in the Table P can be prepared in a manner analogous to the procedures described in the Examples P1 to P9.

Table P

Compound	Structure	MS	¹ H-NMR
T1.3		Electrospray: 536, 538, 540 ((M+H) ⁺).	CDCl ₃ : 8.43 (d, 1H), 7.91 (s, 1H), 7.81 (d, 1H), 7.64 (s, 1H), 7.59 (t, 2H), 7.33 (m, 2H), 7.22 (m, 1H), 6.19 (d, 1H), 4.19 (m, 1H), 1.18 (d, 6H).
T6.1		Electrospray: 474, 476 ((M+H) ⁺).	DMSO-d ₆ : 12.75 (s, 1H), 9.13 (d, 1H), 8.69 (s, 1H), 8.60 (d, 1H), 8.44 (s, 1H), 8.31 (d, 1H), 7.91 (m, 2H), 7.74 (dd, 1H), 7.55 (m, 3H), 2.89 (d, 3H).
T6.3		Electrospray: 502, 504 ((M+H) ⁺).	DMSO-d ₆ : 12.55 (s, 1H), 8.90 (d, 1H), 8.62 (s, 1H), 8.59 (d, 1H), 8.43 (s, 1H), 8.31 (d, 1H), 7.94 (d, 1H), 7.90 (d, 1H), 7.73 (dd, 1H), 7.55 (m, 3H), 4.21 (m, 1H), 1.23 (d, 6H).

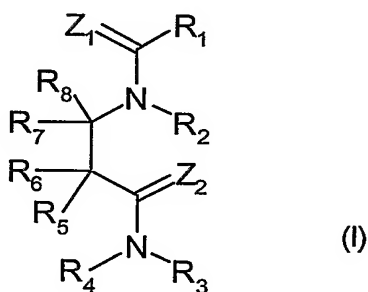
Compound	Structure	MS	¹ H-NMR
T7.1		Electrospray: 552, 554, 556 ((M+H) ⁺).	DMSO-d ₆ : 10.80 (s, 1H), 8.52 (d, 1H), 8.42 (s, 1H), 8.20 (m, 2H), 8.11 (s, 1H), 8.05 (d, 1H), 7.88 (s, 1H), 7.75 (t, 1H), 7.64 (m, 2H), 2.70 (d, 3H).
T7.3		Electrospray: 580, 582, 584 ((M+H) ⁺).	CDCl ₃ : 10.65 (s, 1H), 8.43 (d, 1H), 7.98 (s, 1H), 7.81 (d, 1H), 7.71 (s, 1H), 7.60 (d, 1H), 7.56 (d, 1H), 7.34 (m, 2H), 7.21 (t, 1H), 6.12 (d, 1H), 4.20 (m, 1H), 1.17 (d, 6H).
T21.3		Electrospray: 502, 504 ((M+H) ⁺).	CDCl ₃ : 10.97 (s, 1H), 8.46 (d, 1H), 7.84 (m, 2H), 7.75 (s, 1H), 7.72 (m, 1H), 7.49 (m, 2H), 7.37 (m, 2H), 7.11 (d, 1H), 6.15 (d, 1H), 4.23 (m, 1H), 1.19 (d, 6H).

Example P11

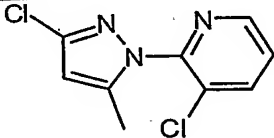
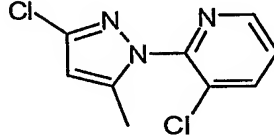
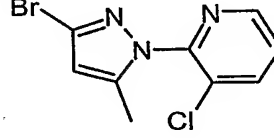
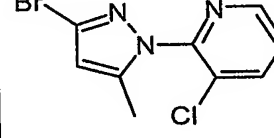
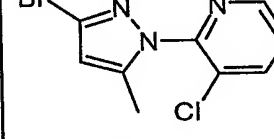
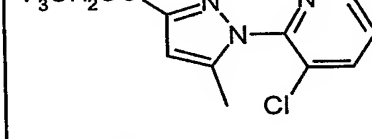
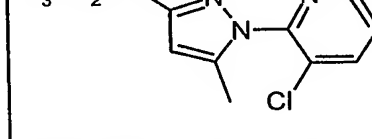
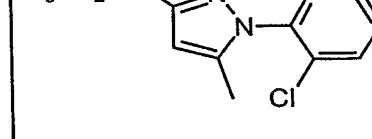
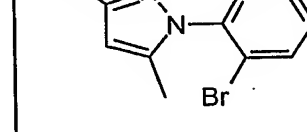
The other compounds listed in the Tables 1 to 71 can also be prepared in a manner analogous to the procedures described in the Examples P1 to P10.

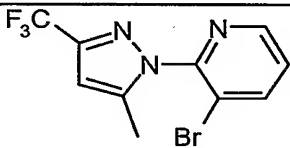
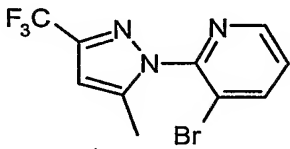
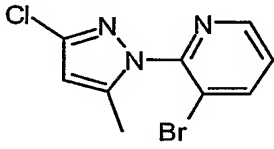
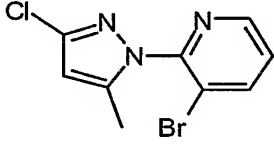
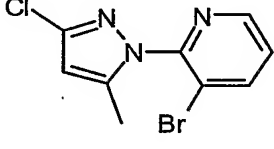
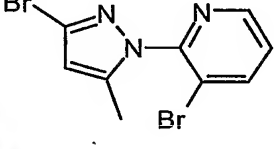
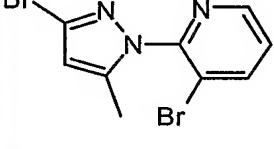
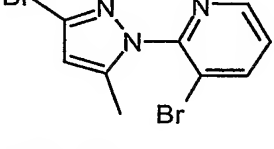
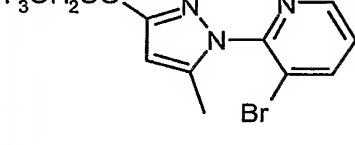
The Table A discloses 206 meanings of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 in a compound of the formula I.

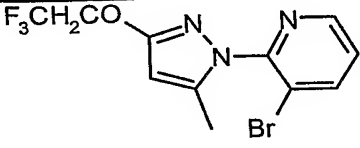
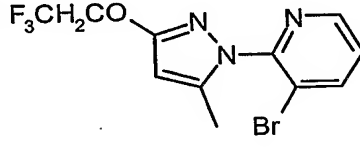
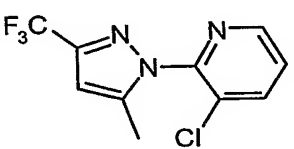
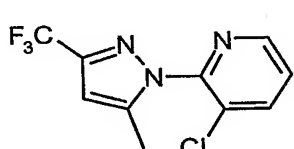
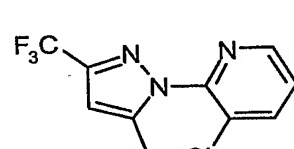
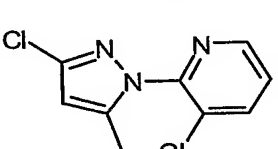
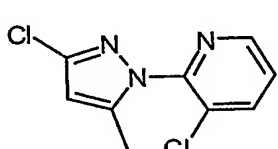
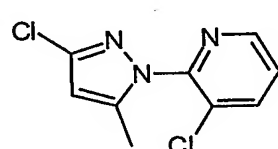
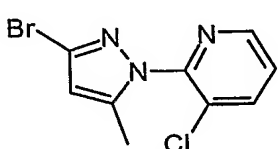
Table A

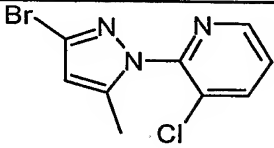
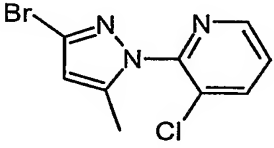
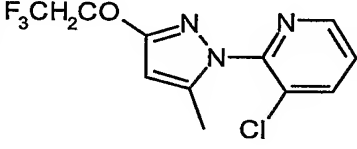
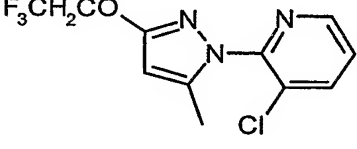
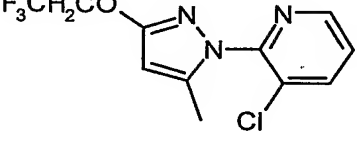
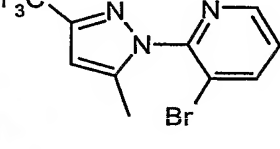
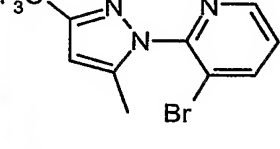
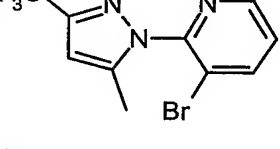
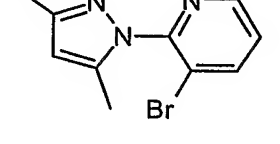


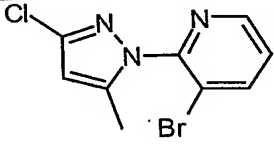
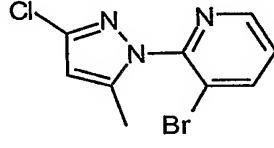
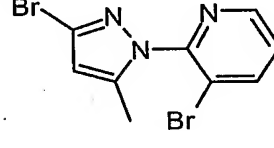
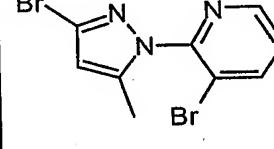
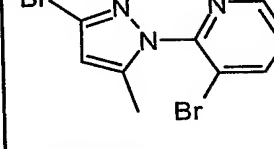
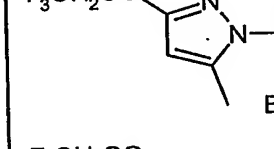
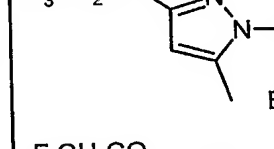

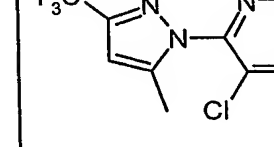
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A.2	O	O		H	H	CH_2CH_3
A.3	O	O		H	H	$\text{CH}(\text{CH}_3)_2$
A.4	O	O		H	H	CH_3

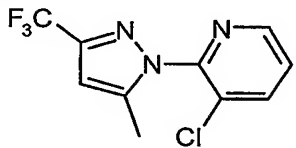
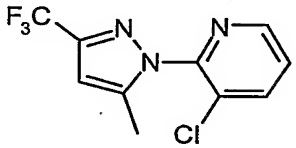
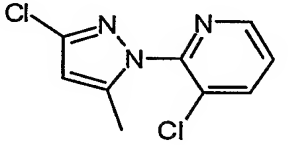
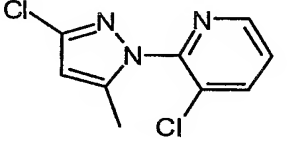
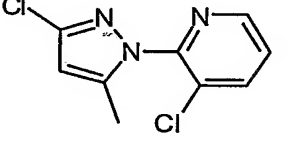
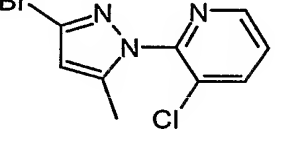
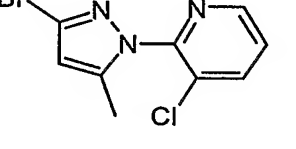
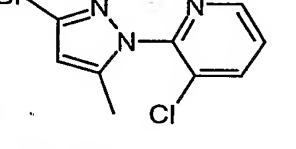
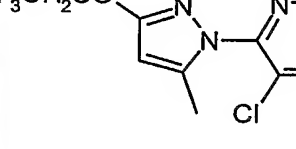
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A.6	O	O		H	H	CH(CH ₃) ₂
A.7	O	O		H	H	CH ₃
A.8	O	O		H	H	CH ₂ CH ₃
A.9	O	O		H	H	CH(CH ₃) ₂
A.10	O	O		H	H	CH ₃
A.11	O	O		H	H	CH ₂ CH ₃
A.12	O	O		H	H	CH(CH ₃) ₂
A.13	O	O		H	H	CH ₃

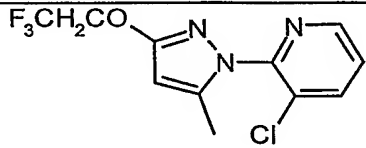
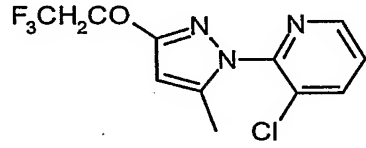
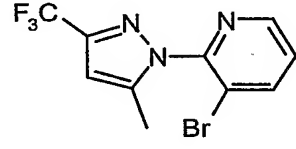
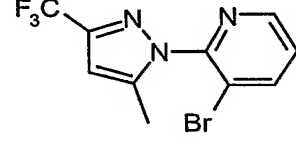
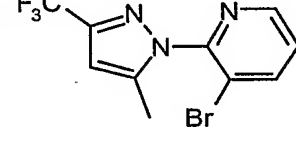
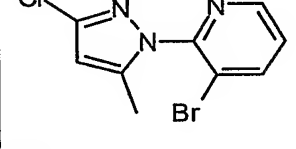
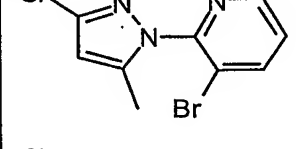
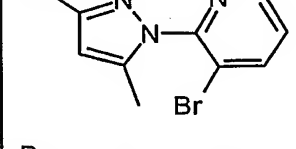
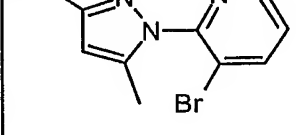
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A.15	O	O		H	H	CH(CH ₃) ₂
A.16	O	O		H	H	CH ₃
A.17	O	O		H	H	CH ₂ CH ₃
A.18	O	O		H	H	CH(CH ₃) ₂
A.19	O	O		H	H	CH ₃
A.20	O	O		H	H	CH ₂ CH ₃
A.21	O	O		H	H	CH(CH ₃) ₂
A.22	O	O		H	H	CH ₃

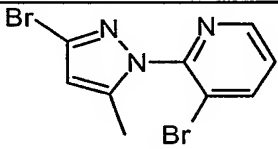
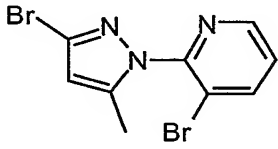
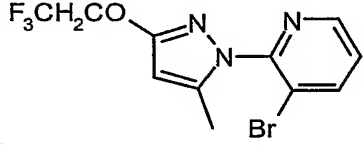
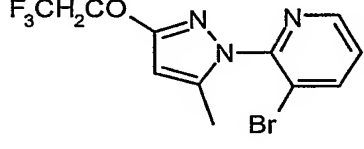
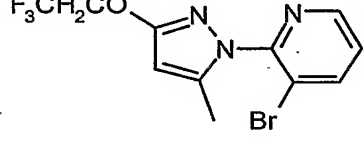
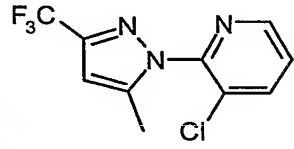
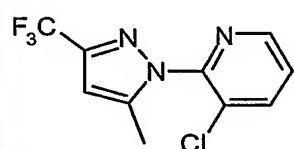
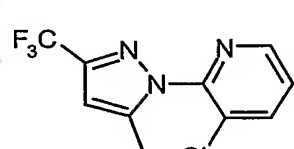
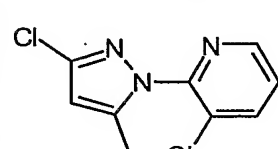
Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.23	O	O		H	H	CH ₂ CH ₃
A.24	O	O		H	H	CH(CH ₃) ₂
A.25	S	S		H	H	CH ₃
A.26	S	S		H	H	CH ₂ CH ₃
A.27	S	S		H	H	CH(CH ₃) ₂
A.28	S	S		H	H	CH ₃
A.29	S	S		H	H	CH ₂ CH ₃
A.30	S	S		H	H	CH(CH ₃) ₂
A.31	S	S		H	H	CH ₃

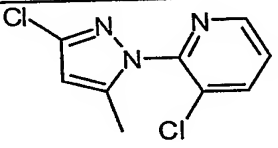
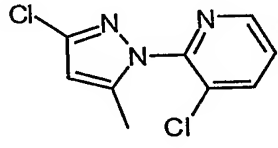
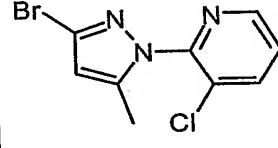
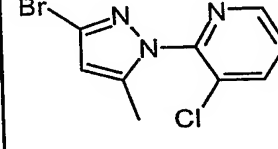
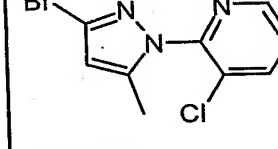
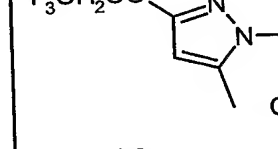
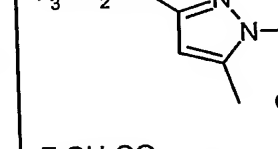
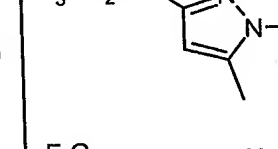
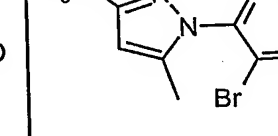
Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.32	S	S		H	H	CH ₂ CH ₃
A.33	S	S		H	H	CH(CH ₃) ₂
A.34	S	S		H	H	CH ₃
A.35	S	S		H	H	CH ₂ CH ₃
A.36	S	S		H	H	CH(CH ₃) ₂
A.37	S	S		H	H	CH ₃
A.38	S	S		H	H	CH ₂ CH ₃
A.39	S	S		H	H	CH(CH ₃) ₂
A.40	S	S		H	H	CH ₃

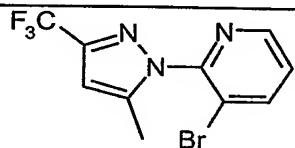
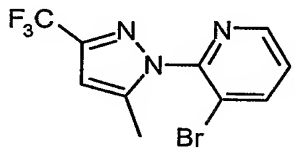
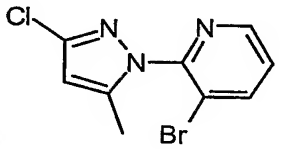
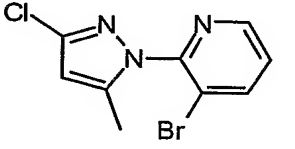
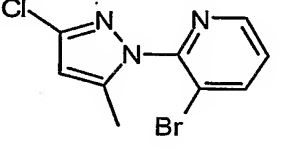
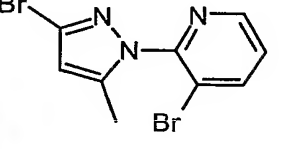
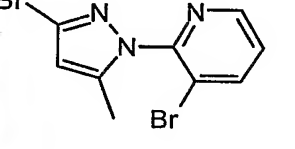
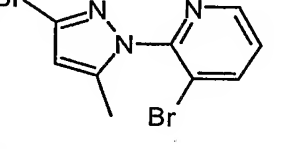
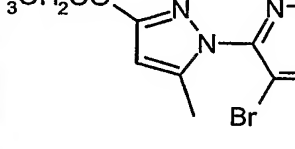
Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.41	S	S		H	H	CH ₂ CH ₃
A.42	S	S		H	H	CH(CH ₃) ₂
A.43	S	S		H	H	CH ₃
A.44	S	S		H	H	CH ₂ CH ₃
A.45	S	S		H	H	CH(CH ₃) ₂
A.46	S	S		H	H	CH ₃
A.47	S	S		H	H	CH ₂ CH ₃
A.48	S	S		H	H	CH(CH ₃) ₂
A.49	O	S		H	H	CH ₃

Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.50	O	S		H	H	CH ₂ CH ₃
A.51	O	S		H	H	CH(CH ₃) ₂
A.52	O	S		H	H	CH ₃
A.53	O	S		H	H	CH ₂ CH ₃
A.54	O	S		H	H	CH(CH ₃) ₂
A.55	O	S		H	H	CH ₃
A.56	O	S		H	H	CH ₂ CH ₃
A.57	O	S		H	H	CH(CH ₃) ₂
A.58	O	S		H	H	CH ₃

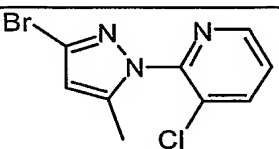
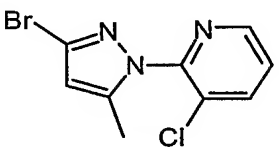
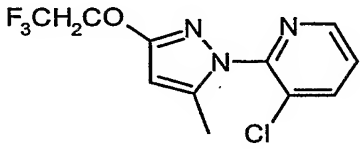
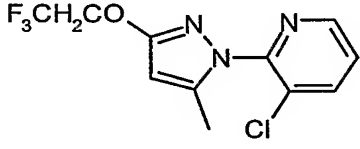
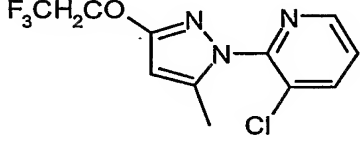
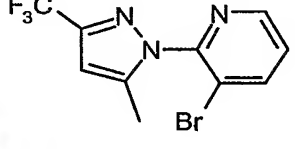
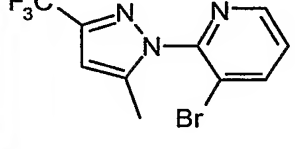
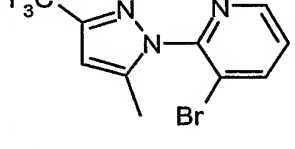
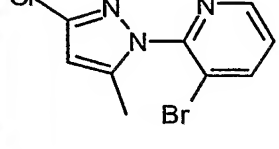
Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.59	O	S		H	H	CH ₂ CH ₃
A.60	O	S		H	H	CH(CH ₃) ₂
A.61	O	S		H	H	CH ₃
A.62	O	S		H	H	CH ₂ CH ₃
A.63	O	S		H	H	CH(CH ₃) ₂
A.64	O	S		H	H	CH ₃
A.65	O	S		H	H	CH ₂ CH ₃
A.66	O	S		H	H	CH(CH ₃) ₂
A.67	O	S		H	H	CH ₃

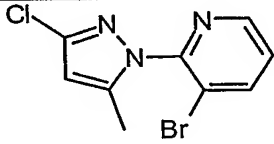
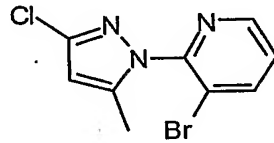
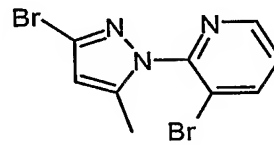
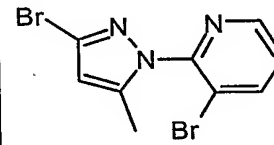
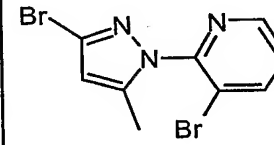
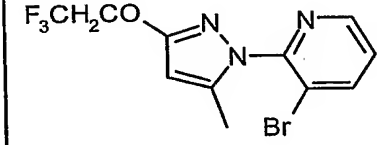
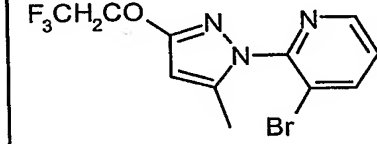
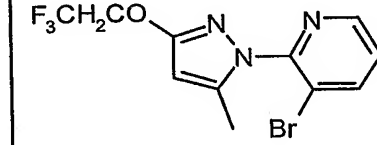
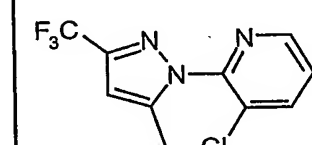
Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.68	O	S		H	H	CH ₂ CH ₃
A.69	O	S		H	H	CH(CH ₃) ₂
A.70	O	S		H	H	CH ₃
A.71	O	S		H	H	CH ₂ CH ₃
A.72	O	S		H	H	CH(CH ₃) ₂
A.73	S	O		H	H	CH ₃
A.74	S	O		H	H	CH ₂ CH ₃
A.75	S	O		H	H	CH(CH ₃) ₂
A.76	S	O		H	H	CH ₃

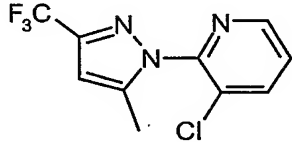
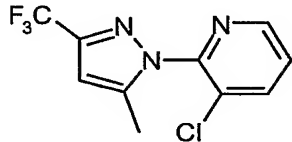
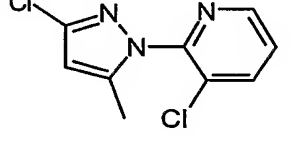
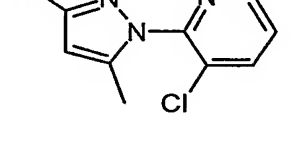
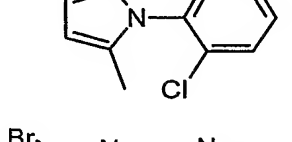
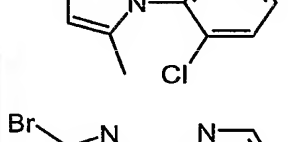
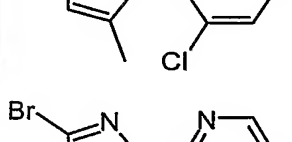
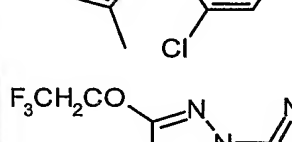

Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.77	S	O		H	H	CH ₂ CH ₃
A.78	S	O		H	H	CH(CH ₃) ₂
A.79	S	O		H	H	CH ₃
A.80	S	O		H	H	CH ₂ CH ₃
A.81	S	O		H	H	CH(CH ₃) ₂
A.82	S	O		H	H	CH ₃
A.83	S	O		H	H	CH ₂ CH ₃
A.84	S	O		H	H	CH(CH ₃) ₂
A.85	S	O		H	H	CH ₃

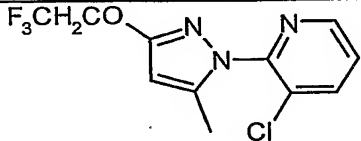
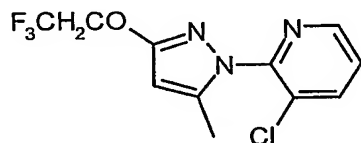
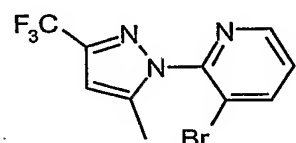
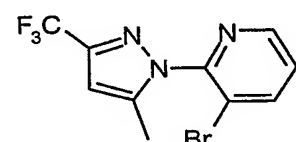
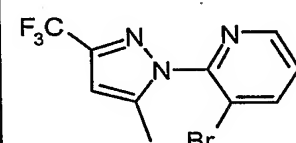
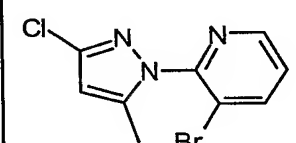
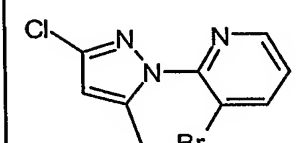
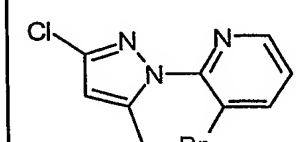
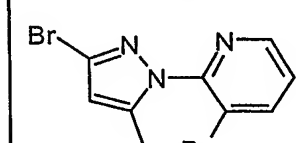
Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.86	S	O		H	H	CH ₂ CH ₃
A.87	S	O		H	H	CH(CH ₃) ₂
A.88	S	O		H	H	CH ₃
A.89	S	O		H	H	CH ₂ CH ₃
A.90	S	O		H	H	CH(CH ₃) ₂
A.91	S	O		H	H	CH ₃
A.92	S	O		H	H	CH ₂ CH ₃
A.93	S	O		H	H	CH(CH ₃) ₂
A.94	S	O		H	H	CH ₃

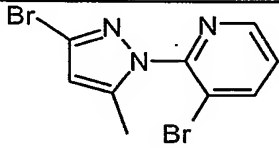
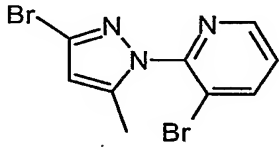
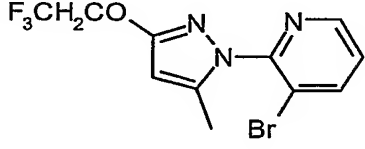
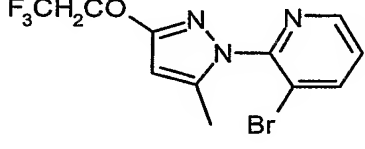
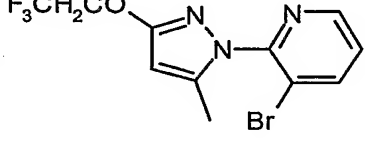
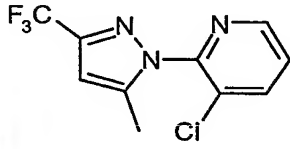
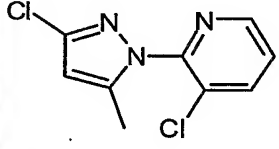
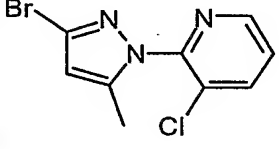
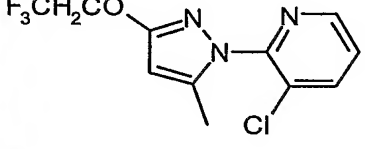
Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.95	S	O		H	H	CH ₂ CH ₃
A.96	S	O		H	H	CH(CH ₃) ₂
A.97	O	O		CH ₃	H	CH ₃
A.98	O	O		CH ₃	H	CH ₂ CH ₃
A.99	O	O		CH ₃	H	CH(CH ₃) ₂
A.100	O	O		CH ₃	H	CH ₃
A.101	O	O		CH ₃	H	CH ₂ CH ₃
A.102	O	O		CH ₃	H	CH(CH ₃) ₂
A.103	O	O		CH ₃	H	CH ₃

Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.104	O	O		CH ₃	H	CH ₂ CH ₃
A.105	O	O		CH ₃	H	CH(CH ₃) ₂
A.106	O	O		CH ₃	H	CH ₃
A.107	O	O		CH ₃	H	CH ₂ CH ₃
A.108	O	O		CH ₃	H	CH(CH ₃) ₂
A.109	O	O		CH ₃	H	CH ₃
A.110	O	O		CH ₃	H	CH ₂ CH ₃
A.111	O	O		CH ₃	H	CH(CH ₃) ₂
A.112	O	O		CH ₃	H	CH ₃

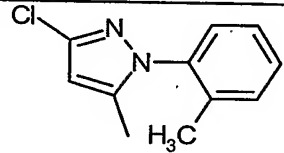
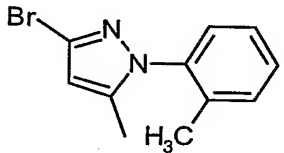
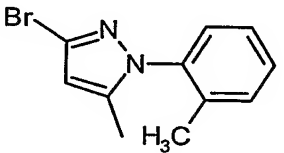
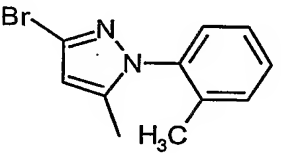
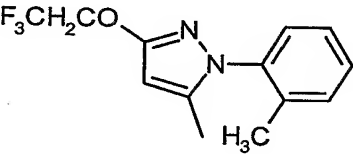
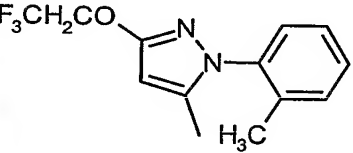
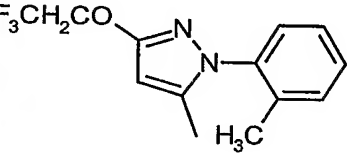
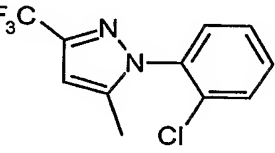
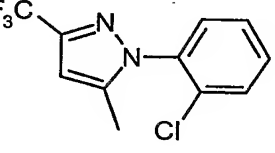
Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.113	O	O		CH ₃	H	CH ₂ CH ₃
A.114	O	O		CH ₃	H	CH(CH ₃) ₂
A.115	O	O		CH ₃	H	CH ₃
A.116	O	O		CH ₃	H	CH ₂ CH ₃
A.117	O	O		CH ₃	H	CH(CH ₃) ₂
A.118	O	O		CH ₃	H	CH ₃
A.119	O	O		CH ₃	H	CH ₂ CH ₃
A.120	O	O		CH ₃	H	CH(CH ₃) ₂
A.121	O	O		H	CH ₃	CH ₃

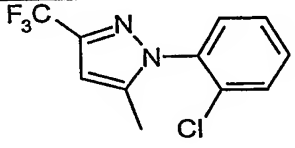
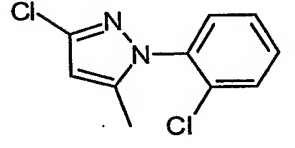
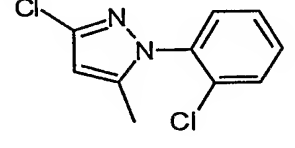
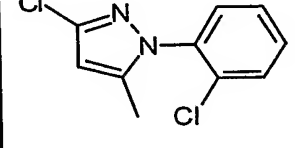
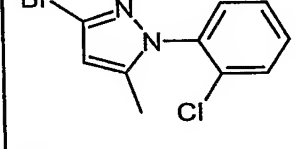
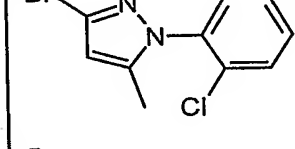
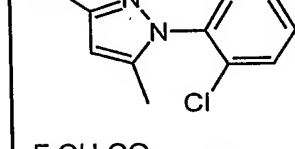
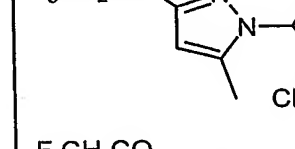
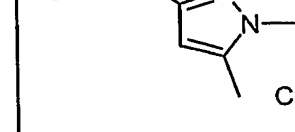
Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.122	O	O		H	CH ₃	CH ₂ CH ₃
A.123	O	O		H	CH ₃	CH(CH ₃) ₂
A.124	O	O		H	CH ₃	CH ₃
A.125	O	O		H	CH ₃	CH ₂ CH ₃
A.126	O	O		H	CH ₃	CH(CH ₃) ₂
A.127	O	O		H	CH ₃	CH ₃
A.128	O	O		H	CH ₃	CH ₂ CH ₃
A.129	O	O		H	CH ₃	CH(CH ₃) ₂
A.130	O	O		H	CH ₃	CH ₃

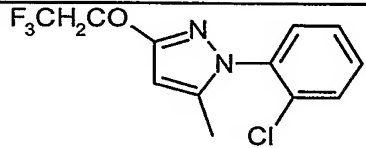
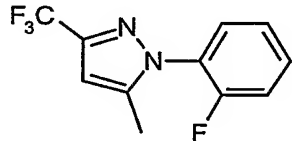
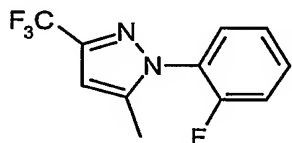
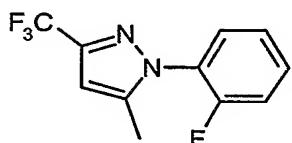
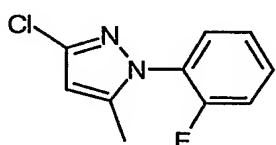
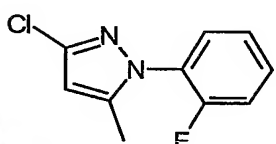
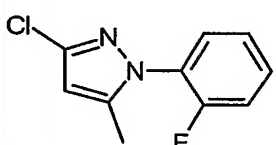
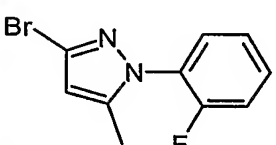
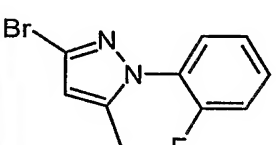
Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.131	O	O		H	CH ₃	CH ₂ CH ₃
A.132	O	O		H	CH ₃	CH(CH ₃) ₂
A.133	O	O		H	CH ₃	CH ₃
A.134	O	O		H	CH ₃	CH ₂ CH ₃
A.135	O	O		H	CH ₃	CH(CH ₃) ₂
A.136	O	O		H	CH ₃	CH ₃
A.137	O	O		H	CH ₃	CH ₂ CH ₃
A.138	O	O		H	CH ₃	CH(CH ₃) ₂
A.139	O	O		H	CH ₃	CH ₃

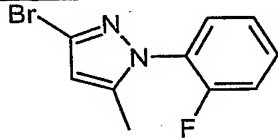
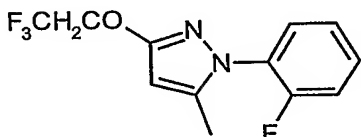
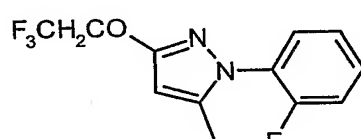
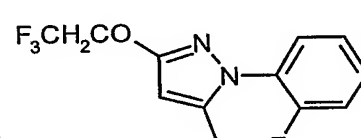
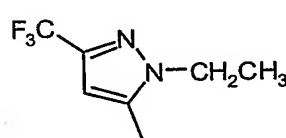
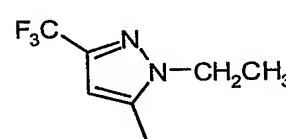
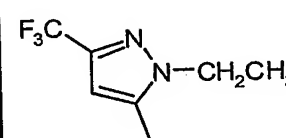
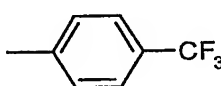
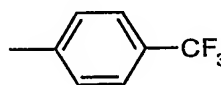
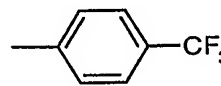
Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.140	O	O		H	CH ₃	CH ₂ CH ₃
A.141	O	O		H	CH ₃	CH(CH ₃) ₂
A.142	O	O		H	CH ₃	CH ₃
A.143	O	O		H	CH ₃	CH ₂ CH ₃
A.144	O	O		H	CH ₃	CH(CH ₃) ₂
A.145	O	O		H	H	C(CH ₃) ₃
A.146	O	O		H	H	C(CH ₃) ₃
A.147	O	O		H	H	C(CH ₃) ₃
A.148	O	O		H	H	C(CH ₃) ₃

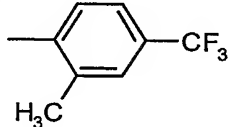
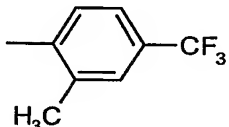
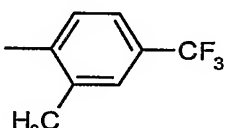
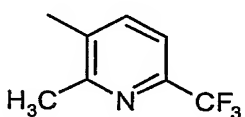
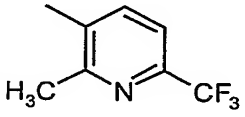
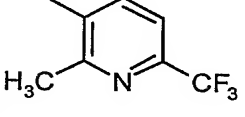
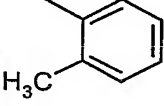
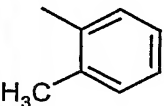
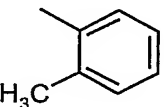
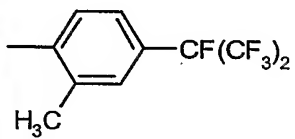
Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.149	O	O		H	H	C(CH ₃) ₃
A.150	O	O		H	H	C(CH ₃) ₃
A.151	O	O		H	H	C(CH ₃) ₃
A.152	O	O		H	H	C(CH ₃) ₃
A.153	O	O		H	H	CH ₃
A.154	O	O		H	H	CH ₂ CH ₃
A.155	O	O		H	H	CH(CH ₃) ₂
A.156	O	O		H	H	CH ₃
A.157	O	O		H	H	CH ₂ CH ₃

Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.158	O	O		H	H	CH(CH ₃) ₂
A.159	O	O		H	H	CH ₃
A.160	O	O		H	H	CH ₂ CH ₃
A.161	O	O		H	H	CH(CH ₃) ₂
A.162	O	O		H	H	CH ₃
A.163	O	O		H	H	CH ₂ CH ₃
A.164	O	O		H	H	CH(CH ₃) ₂
A.165	O	O		H	H	CH ₃
A.166	O	O		H	H	CH ₂ CH ₃

Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.167	O	O		H	H	CH(CH ₃) ₂
A.168	O	O		H	H	CH ₃
A.169	O	O		H	H	CH ₂ CH ₃
A.170	O	O		H	H	CH(CH ₃) ₂
A.171	O	O		H	H	CH ₃
A.172	O	O		H	H	CH ₂ CH ₃
A.173	O	O		H	H	CH(CH ₃) ₂
A.174	O	O		H	H	CH ₃
A.175	O	O		H	H	CH ₂ CH ₃

Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.176	O	O		H	H	CH(CH ₃) ₂
A.177	O	O		H	H	CH ₃
A.178	O	O		H	H	CH ₂ CH ₃
A.179	O	O		H	H	CH(CH ₃) ₂
A.180	O	O		H	H	CH ₃
A.181	O	O		H	H	CH ₂ CH ₃
A.182	O	O		H	H	CH(CH ₃) ₂
A.183	O	O		H	H	CH ₃
A.184	O	O		H	H	CH ₂ CH ₃

Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.185	O	O		H	H	CH(CH ₃) ₂
A.186	O	O		H	H	CH ₃
A.187	O	O		H	H	CH ₂ CH ₃
A.188	O	O		H	H	CH(CH ₃) ₂
A.189	O	O		H	H	CH ₃
A.190	O	O		H	H	CH ₂ CH ₃
A.191	O	O		H	H	CH(CH ₃) ₂
A.192	O	O		H	H	CH ₃
A.193	O	O		H	H	CH ₂ CH ₃
A.194	O	O		H	H	CH(CH ₃) ₂

Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.195	O	O		H	H	CH ₃
A.196	O	O		H	H	CH ₂ CH ₃
A.197	O	O		H	H	CH(CH ₃) ₂
A.198	O	O		H	H	CH ₃
A.199	O	O		H	H	CH ₂ CH ₃
A.200	O	O		H	H	CH(CH ₃) ₂
A.201	O	O		H	H	CH ₃
A.202	O	O		H	H	CH ₂ CH ₃
A.203	O	O		H	H	CH(CH ₃) ₂
A.204	O	O		H	H	CH ₃

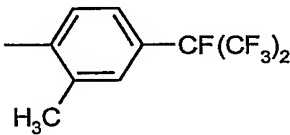
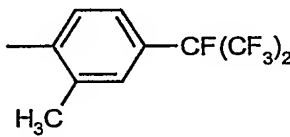
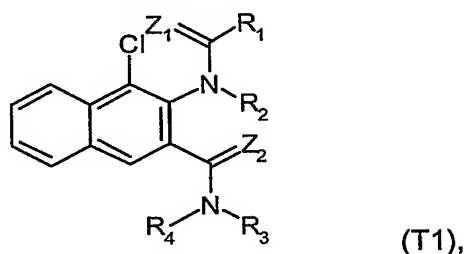
Line	Z ₁	Z ₂	-R ₁	R ₂	R ₃	R ₄
A.205	O	O		H	H	CH ₂ CH ₃
A.206	O	O		H	H	CH(CH ₃) ₂

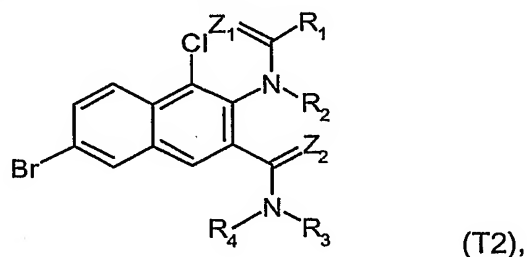
Table 1: This table discloses the 206 compounds T1.1 to T1.206 of the formula



in which, for each of these 206 specific compounds, each of the variables Z₁, Z₂, R₁, R₂, R₃ and R₄ has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

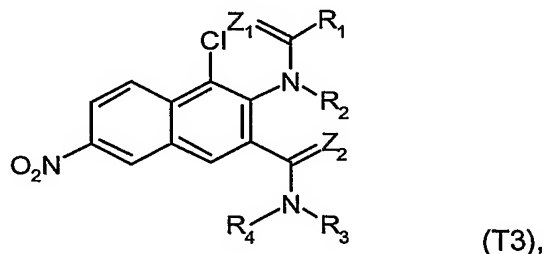
For example, the specific compound T1.23 is the compound of the formula T1, in which each of the variables Z₁, Z₂, R₁, R₂, R₃ and R₄ has the specific meaning given in the line A.23 of the Table A. According to the same system, also all of the other 205 specific compounds disclosed in the Table 1 as well as all of the specific compounds disclosed in the Tables 2 to 71 are specified analogously.

Table 2: This table discloses the 206 compounds T2.1 to T2.206 of the formula



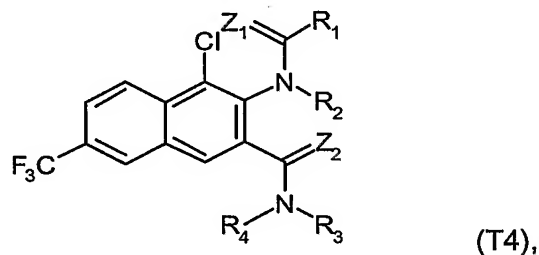
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 3: This table discloses the 206 compounds T3.1 to T3.206 of the formula



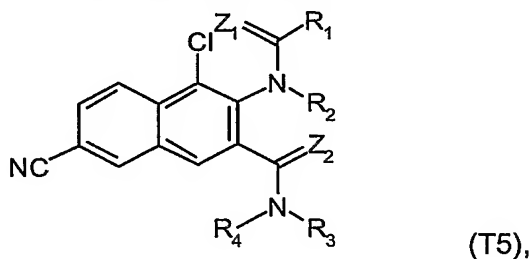
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 4: This table discloses the 206 compounds T4.1 to T4.206 of the formula



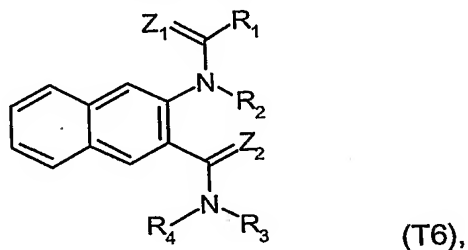
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 5: This table discloses the 206 compounds T5.1 to T5.206 of the formula



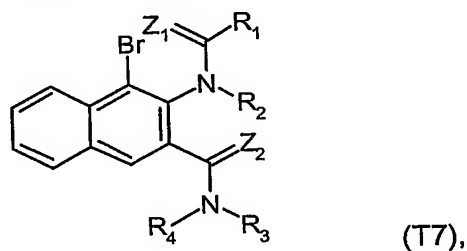
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 6: This table discloses the 206 compounds T6.1 to T6.206 of the formula



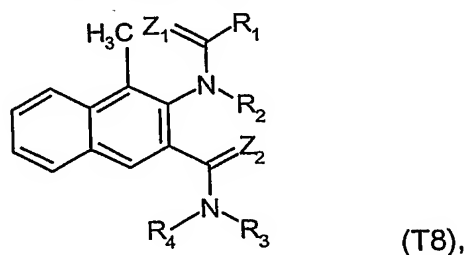
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 7: This table discloses the 206 compounds T7.1 to T7.206 of the formula



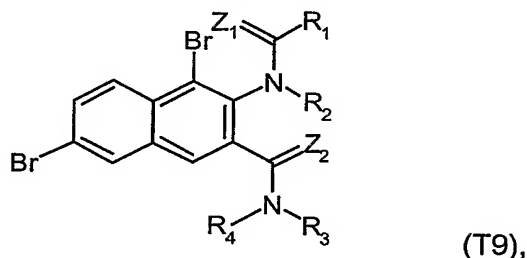
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 8: This table discloses the 206 compounds T8.1 to T8.206 of the formula



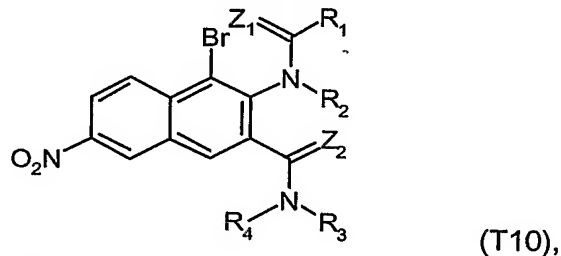
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 9: This table discloses the 206 compounds T9.1 to T9.206 of the formula



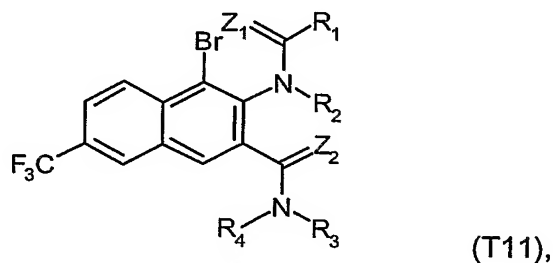
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 10: This table discloses the 206 compounds T10.1 to T10.206 of the formula



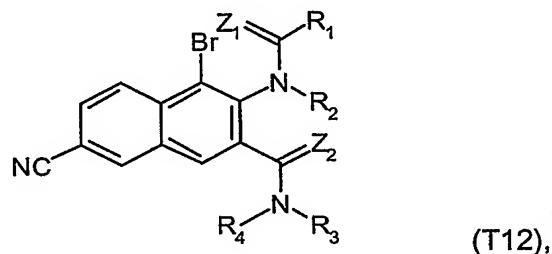
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 11: This table discloses the 206 compounds T11.1 to T11.206 of the formula



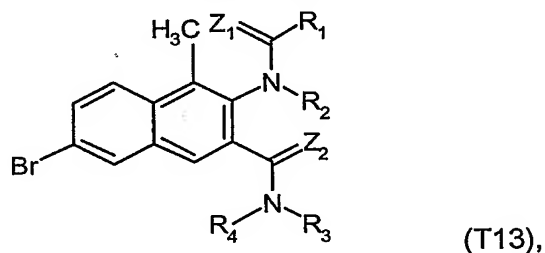
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 12: This table discloses the 206 compounds T12.1 to T12.206 of the formula



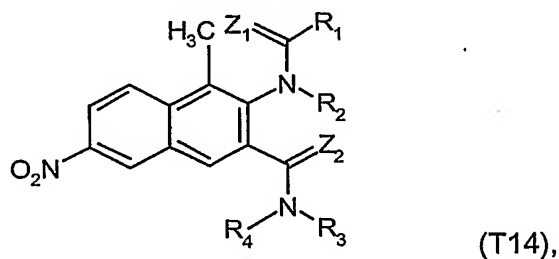
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 13: This table discloses the 206 compounds T13.1 to T13.206 of the formula



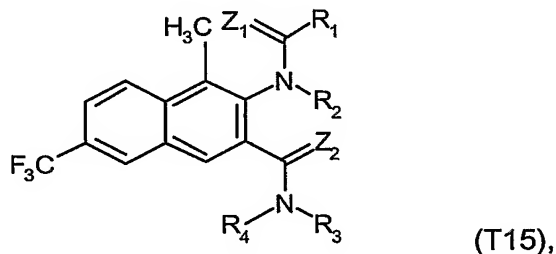
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 14: This table discloses the 206 compounds T14.1 to T14.206 of the formula



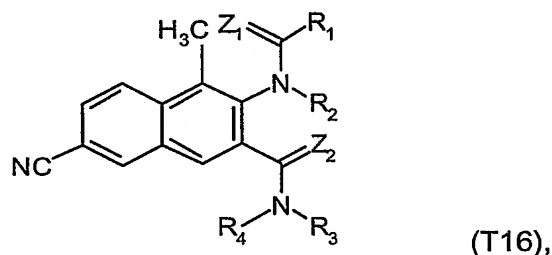
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 15: This table discloses the 206 compounds T15.1 to T15.206 of the formula



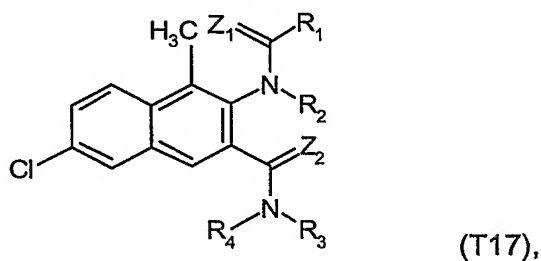
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 16: This table discloses the 206 compounds T16.1 to T16.206 of the formula



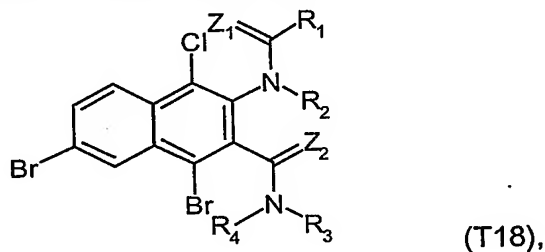
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 17: This table discloses the 206 compounds T17.1 to T17.206 of the formula



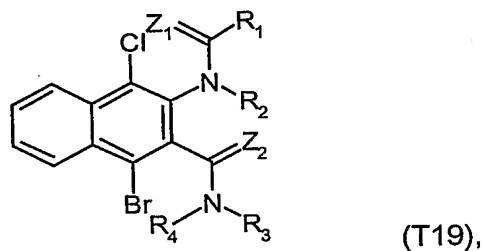
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 18: This table discloses the 206 compounds T18.1 to T18.206 of the formula



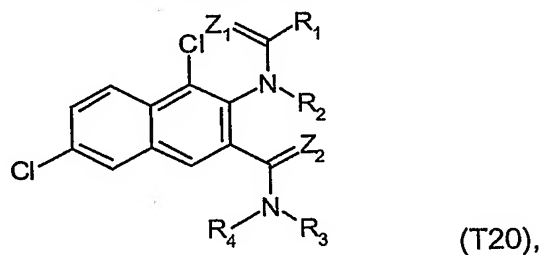
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 19: This table discloses the 206 compounds T19.1 to T19.206 of the formula



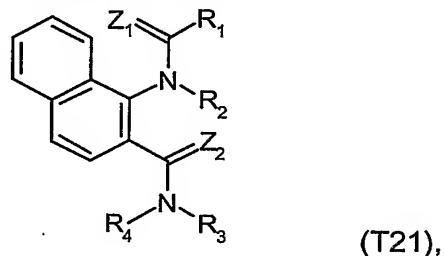
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 20: This table discloses the 206 compounds T20.1 to T20.206 of the formula



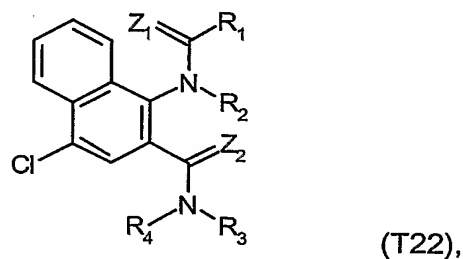
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 21: This table discloses the 206 compounds T21.1 to T21.206 of the formula



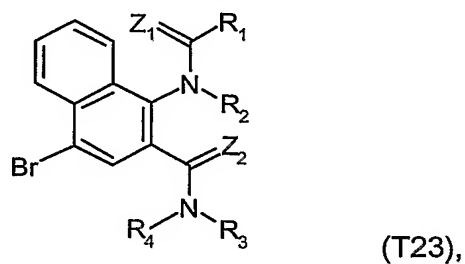
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 22: This table discloses the 206 compounds T22.1 to T22.206 of the formula



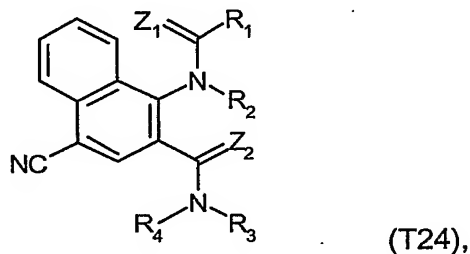
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 23: This table discloses the 206 compounds T23.1 to T23.206 of the formula



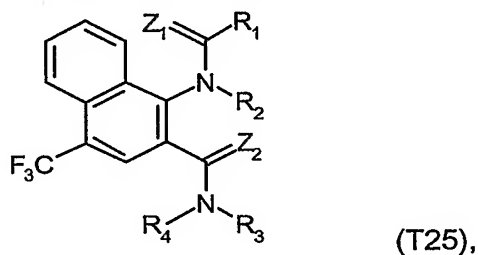
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 24: This table discloses the 206 compounds T24.1 to T24.206 of the formula



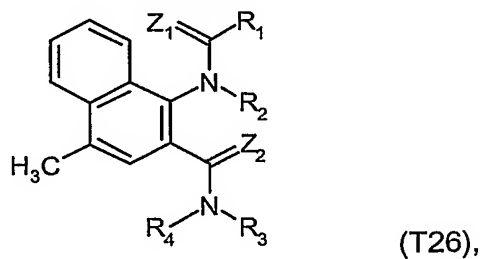
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 25: This table discloses the 206 compounds T25.1 to T25.206 of the formula



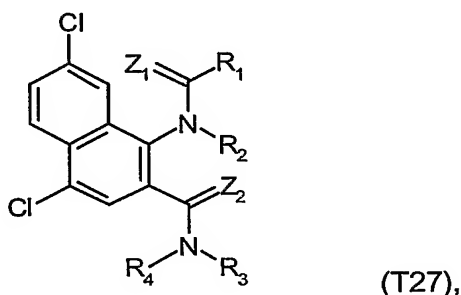
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 26: This table discloses the 206 compounds T26.1 to T26.206 of the formula



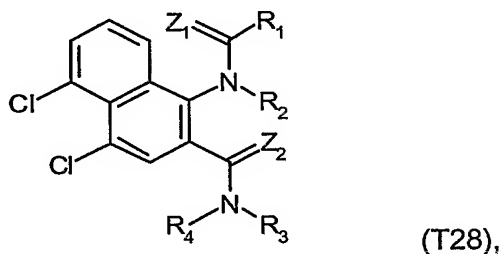
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 27: This table discloses the 206 compounds T27.1 to T27.206 of the formula



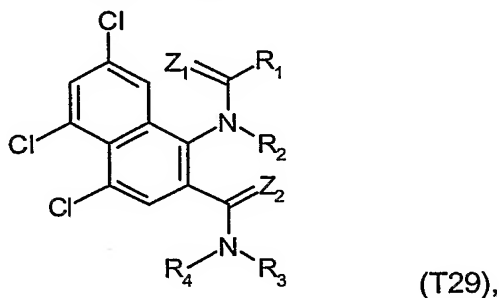
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 28: This table discloses the 206 compounds T28.1 to T28.206 of the formula



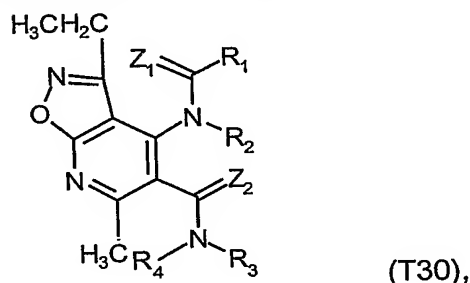
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 29: This table discloses the 206 compounds T29.1 to T29.206 of the formula



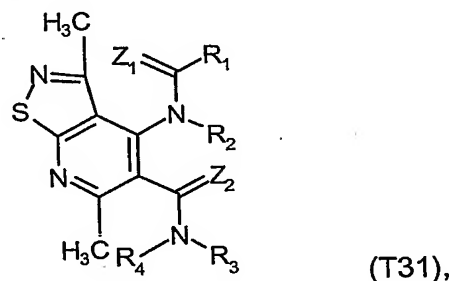
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 30: This table discloses the 206 compounds T30.1 to T30.206 of the formula



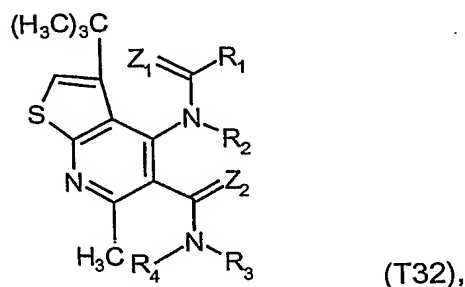
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 31: This table discloses the 206 compounds T31.1 to T31.206 of the formula



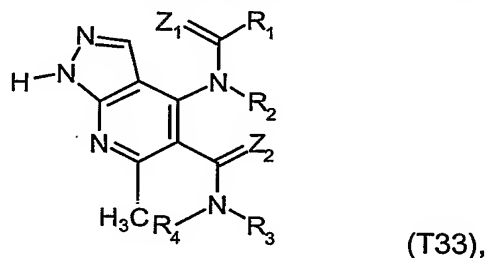
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 32: This table discloses the 206 compounds T32.1 to T32.206 of the formula



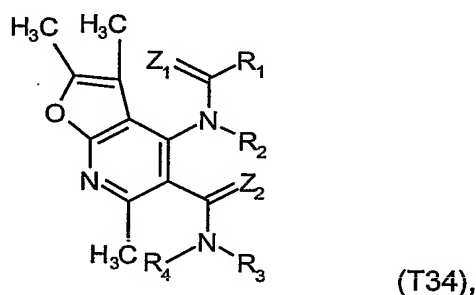
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 33: This table discloses the 206 compounds T33.1 to T33.206 of the formula



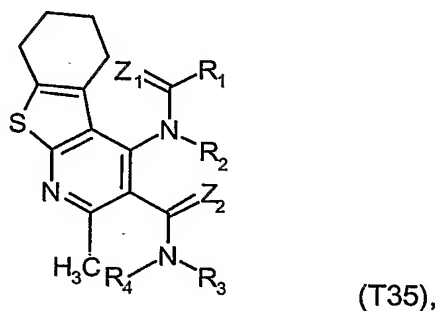
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 34: This table discloses the 206 compounds T34.1 to T34.206 of the formula



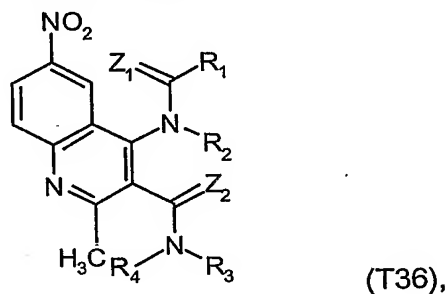
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 35: This table discloses the 206 compounds T35.1 to T35.206 of the formula



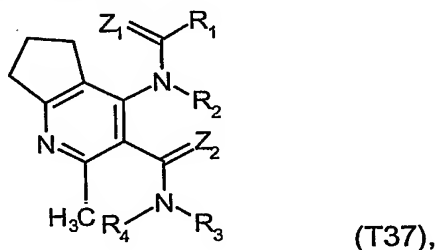
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 36: This table discloses the 206 compounds T36.1 to T36.206 of the formula



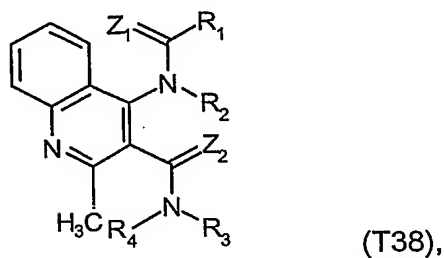
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 37: This table discloses the 206 compounds T37.1 to T37.206 of the formula



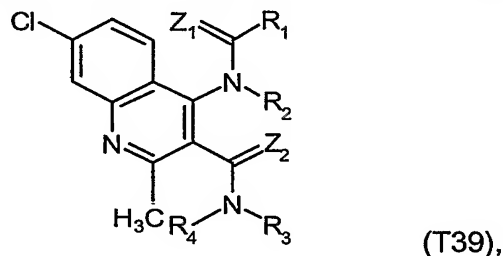
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 38: This table discloses the 206 compounds T38.1 to T38.206 of the formula



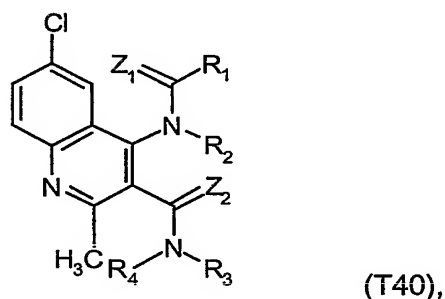
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 39: This table discloses the 206 compounds T39.1 to T39.206 of the formula



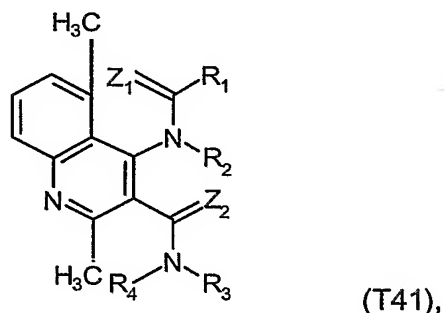
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 40: This table discloses the 206 compounds T40.1 to T40.206 of the formula



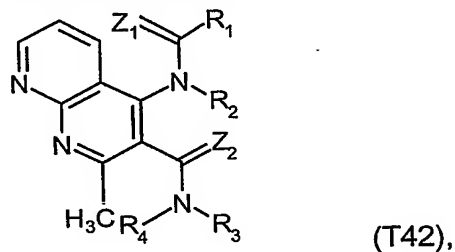
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 41: This table discloses the 206 compounds T41.1 to T41.206 of the formula



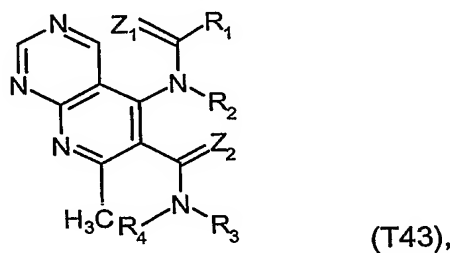
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 42: This table discloses the 206 compounds T42.1 to T42.206 of the formula



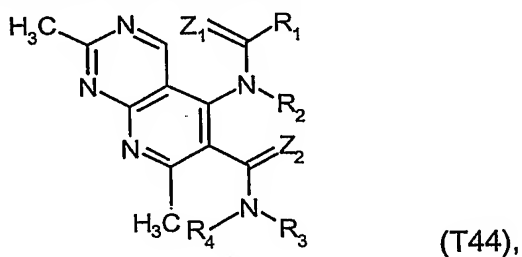
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 43: This table discloses the 206 compounds T43.1 to T43.206 of the formula



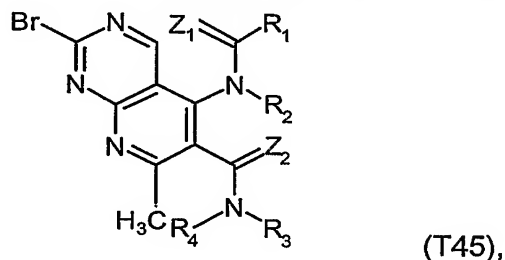
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 44: This table discloses the 206 compounds T44.1 to T44.206 of the formula



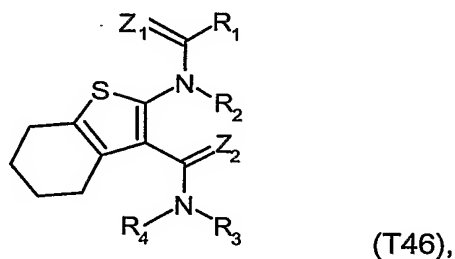
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 45: This table discloses the 206 compounds T45.1 to T45.206 of the formula



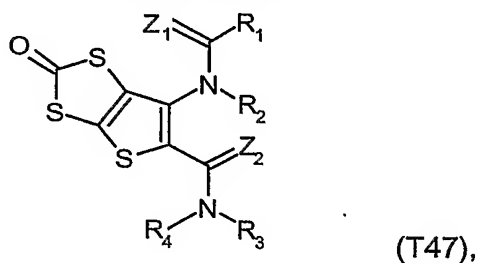
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 46: This table discloses the 206 compounds T46.1 to T46.206 of the formula



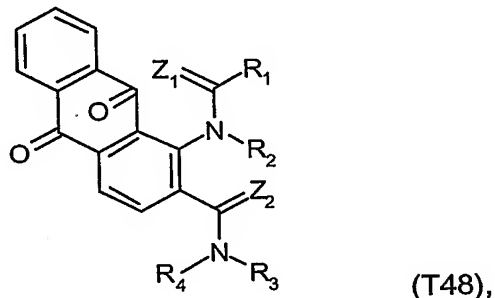
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 47: This table discloses the 206 compounds T47.1 to T47.206 of the formula



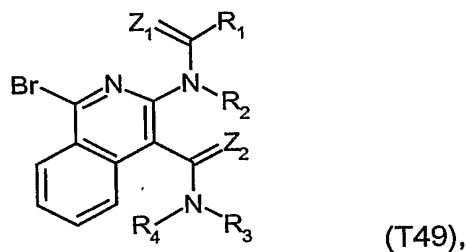
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 48: This table discloses the 206 compounds T48.1 to T48.206 of the formula



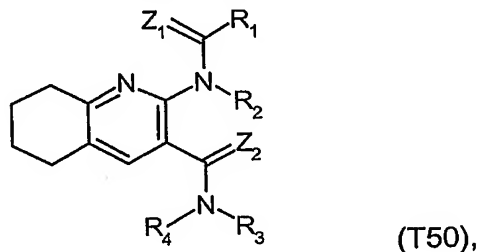
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 49: This table discloses the 206 compounds T49.1 to T49.206 of the formula



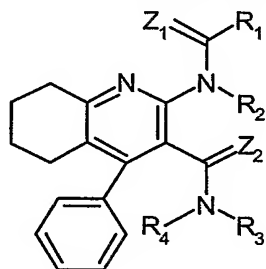
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 50: This table discloses the 206 compounds T50.1 to T50.206 of the formula



in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

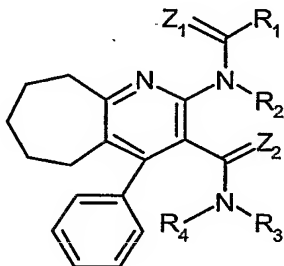
Table 51: This table discloses the 206 compounds T51.1 to T51.206 of the formula



(T51),

in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

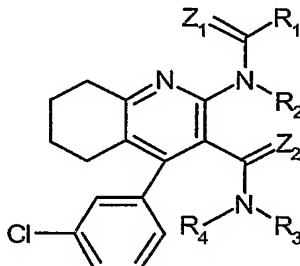
Table 52: This table discloses the 206 compounds T52.1 to T52.206 of the formula



(T52),

in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

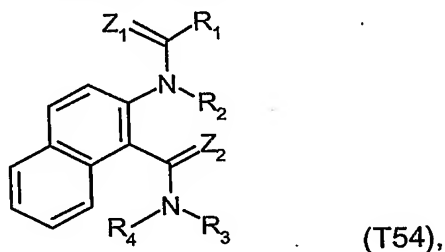
Table 53: This table discloses the 206 compounds T53.1 to T53.206 of the formula



(T53),

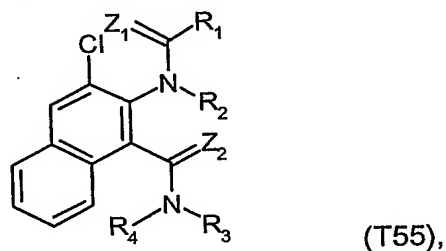
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 54: This table discloses the 206 compounds T54.1 to T54.206 of the formula



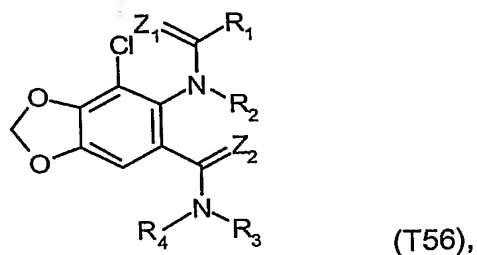
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 55: This table discloses the 206 compounds T55.1 to T55.206 of the formula



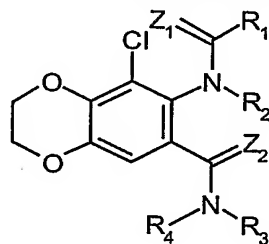
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 56: This table discloses the 206 compounds T56.1 to T56.206 of the formula



in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

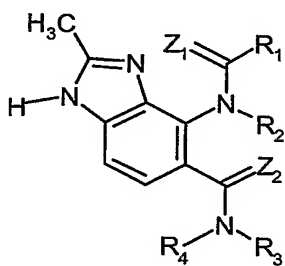
Table 57: This table discloses the 206 compounds T57.1 to T57.206 of the formula



(T57),

in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

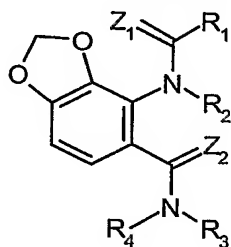
Table 58: This table discloses the 206 compounds T58.1 to T58.206 of the formula



(T58),

in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

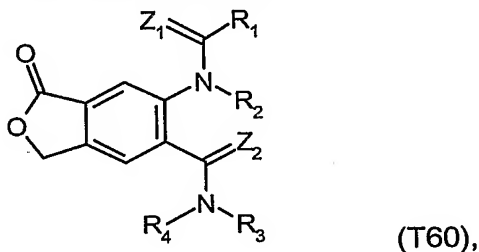
Table 59: This table discloses the 206 compounds T59.1 to T59.206 of the formula



(T59),

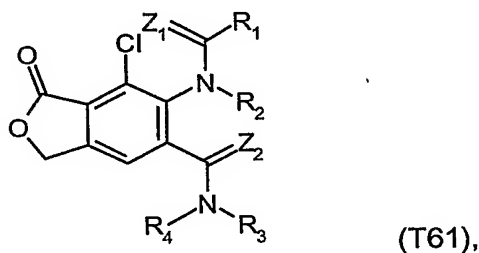
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 60: This table discloses the 206 compounds T60.1 to T60.206 of the formula



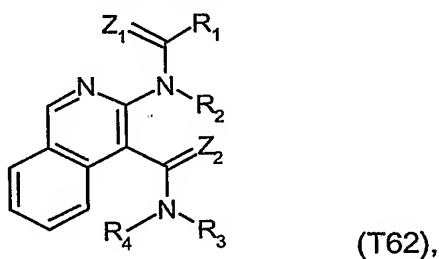
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 61: This table discloses the 206 compounds T61.1 to T61.206 of the formula



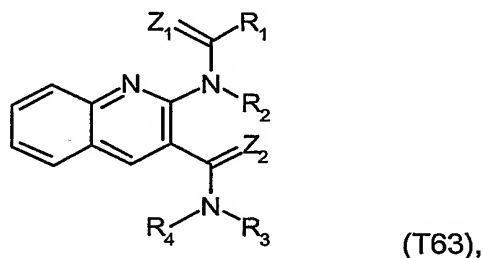
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 62: This table discloses the 206 compounds T62.1 to T62.206 of the formula



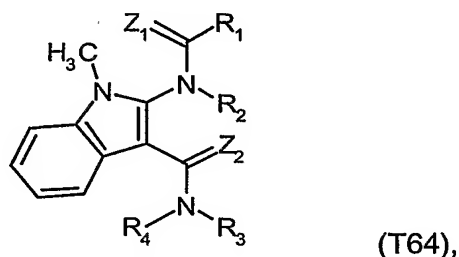
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 63: This table discloses the 206 compounds T63.1 to T63.206 of the formula



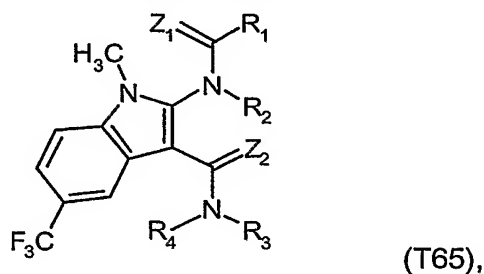
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 64: This table discloses the 206 compounds T64.1 to T64.206 of the formula



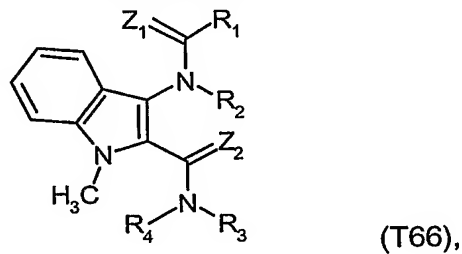
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 65: This table discloses the 206 compounds T65.1 to T65.206 of the formula



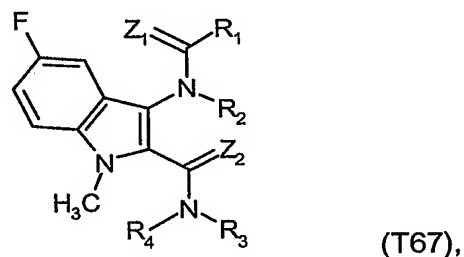
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 66: This table discloses the 206 compounds T66.1 to T66.206 of the formula



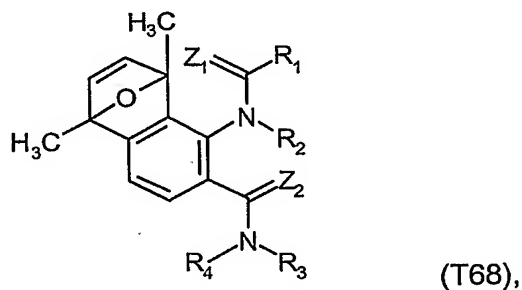
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 67: This table discloses the 206 compounds T67.1 to T67.206 of the formula



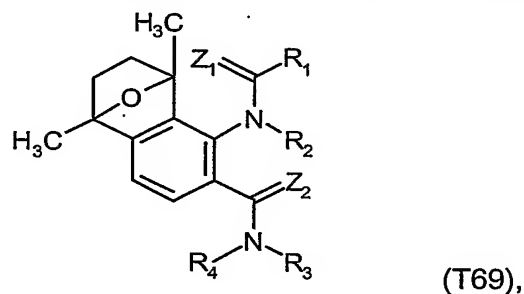
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 68: This table discloses the 206 compounds T68.1 to T68.206 of the formula



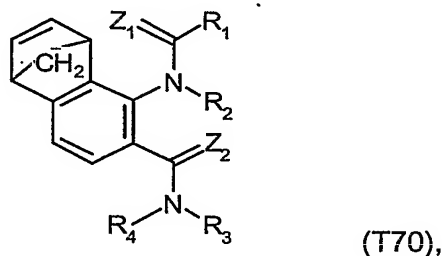
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 69: This table discloses the 206 compounds T69.1 to T69.206 of the formula



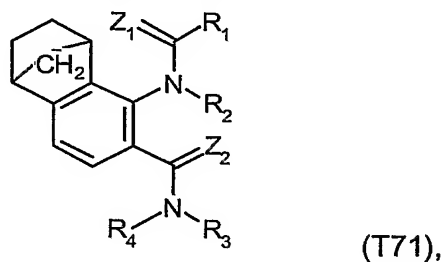
in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 70: This table discloses the 206 compounds T70.1 to T70.206 of the formula



in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Table 71: This table discloses the 206 compounds T71.1 to T71.206 of the formula



in which, for each of these 206 specific compounds, each of the variables Z_1 , Z_2 , R_1 , R_2 , R_3 and R_4 has the specific meaning given in the corresponding line, appropriately selected from the 206 lines A.1 to A.206, of the Table A.

Formulation Examples (% = per cent by weight)

Example F1: Emulsion concentrates

	a)	b)	c)
Active ingredient	25 %	40 %	50 %
Calcium dodecylbenzenesulfonate	5 %	8 %	6 %
Castor oil polyethylene glycol ether (36 mol of EO)	5 %	-	-
Tributylphenoxypolyethylene glycol ether (30 mol of EO)	-	12 %	4 %
Cyclohexanone	-	15 %	20 %
Xylene mixture	65 %	25 %	20 %

Emulsions of any desired concentration can be prepared from such concentrates by dilution with water.

Example F2: Solutions

	a)	b)	c)	d)
Active ingredient	80 %	10 %	5 %	95 %
Ethylene glycol monomethyl ether	20 %	-	-	-
Polyethylene glycol MW 400	-	70 %	-	-
N-Methylpyrrolid-2-one	-	20 %	-	-
Epoxidized coconut oil	-	-	1 %	5 %
Petroleum ether (boiling range: 160-190°)	-	-	94 %	-

The solutions are suitable for use in the form of microdrops.

Example F3: Granules

	a)	b)	c)	d)
Active ingredient	5 %	10 %	8 %	21 %
Kaolin	94 %	-	79 %	54 %
Highly disperse silica	1 %	-	13 %	7 %
Attapulgate	-	90 %	-	18 %

The active ingredient is dissolved in dichloromethane, the solution is sprayed onto the carrier(s), and the solvent is subsequently evaporated in vacuo.

Example F4: Dusts

	a)	b)
Active ingredient	2 %	5 %
Highly disperse silica	1 %	5 %
Talc	97 %	-
Kaolin	-	90 %

Ready-to-use dusts are obtained by intimately mixing the carriers and the active ingredient.

Example F5: Wettable powders

	a)	b)	c)
Active ingredient	25 %	50 %	75 %
Sodium lignosulfonate	5 %	5 %	-
Sodium lauryl sulfate	3 %	-	5 %
Sodium diisobutyl naphthalenesulfonate	-	6 %	10 %
Octylphenoxypolyethylene glycol ether (7-8 mol of EO)	-	2 %	-
Highly disperse silica	5 %	10 %	10 %
Kaolin	62 %	27 %	-

The active ingredient is mixed with the additives and the mixture is ground thoroughly in a suitable mill. This gives wettable powders, which can be diluted with water to give suspensions of any desired concentration.

Example F6: Extruder granules

Active ingredient	10 %
Sodium lignosulfonate	2 %
Carboxymethylcellulose	1 %
Kaolin	87 %

The active ingredient is mixed with the additives, and the mixture is ground, moistened with water, extruded, granulated and dried in a stream of air.

Example F7: Coated granules

Active ingredient	3 %
Polyethylene glycol (MW 200)	3 %
Kaolin	94 %

In a mixer, the finely ground active ingredient is applied uniformly to the kaolin, which has been moistened with the polyethylene glycol. This gives dust-free coated granules.

Example F8: Suspension concentrate

Active ingredient	40 %
Ethylene glycol	10 %
Nonylphenoxypolyethylene glycol ether (15 mol of EO)	6 %
Sodium lignosulfonate	10 %
Carboxymethylcellulose	1 %
37 % aqueous formaldehyde solution	0.2 %
Silicone oil (75 % aqueous emulsion)	0.8 %
Water	32 %

The finely ground active ingredient is mixed intimately with the additives. Suspensions of any desired concentration can be prepared from the thus resulting suspension concentrate by dilution with water.

Biological Examples (% = per cent by weight, unless otherwise specified)Example B1: Activity against Aphis craccivora

Pea seedlings are infected with Aphis craccivora, subsequently sprayed with a spray mixture comprising 400 ppm of active ingredient and then incubated at 20°. 3 and 6 days later, the percentage reduction in the population (% activity) is determined by comparing the number of dead aphids between the treated and untreated plants.

In this test, compounds listed in the Tables 1 to 71 show good activity.

Example B2: Activity against Diabrotica balteata

Maize seedlings are sprayed with an aqueous emulsion spray mixture comprising 400 ppm of active ingredient and, after the spray coating has dried on, populated with 10 larvae (2nd instar) of *Diabrotica balteata* and introduced into a plastic container. 6 days later, the percentage reduction in the population (% activity) is determined by comparing the number of dead larvae between the treated and untreated plants.

In this test, compounds listed in the Tables 1 to 71 show good activity. In particular, the compounds T1.1, T1.3, T7.1 and T7.3 have an activity of over 80 %.

Example B3: Activity against *Heliothis virescens* (foliar application)

Young soya plants are sprayed with an aqueous emulsion spray mixture comprising 400 ppm of active ingredient and, after the spray coating has dried on, populated with 10 caterpillars (1st instar) of *Heliothis virescens* and introduced into a plastic container. 6 days later, the percentage reduction in the population and in the feeding damage (% activity) are determined by comparing the number of dead caterpillars and the feeding damage between the treated and untreated plants.

In this test, compounds listed in the Tables 1 to 71 show good activity. In particular, the compounds T1.1, T1.3, T7.1 and T7.3 have an activity of over 80 %.

Example B4: Activity against *Heliothis virescens* (application to eggs)

Heliothis virescens eggs, which have been deposited on cotton, are sprayed with an aqueous emulsion spray mixture comprising 400 ppm of active ingredient. After 8 days, the percentage hatching rate of the eggs and the survival rate of the caterpillars (% activity) are evaluated in comparison with untreated control batches.

In this test, compounds listed in the Tables 1 to 71 show good activity. In particular, the compounds T1.1, T1.3, T7.1 and T7.3 have an activity of over 80 %.

Example B5: Activity against *Myzus persicae* (foliar application)

Pea seedlings are infected with *Myzus persicae*, subsequently sprayed with a spray mixture comprising 400 ppm of active ingredient and then incubated at 20°. 3 and 6 days later, the percentage reduction in the population (% activity) is determined by comparing the number of dead aphids between the treated and untreated plants.

In this test, compounds listed in the Tables 1 to 71 show good activity. In particular, the compounds T1.1 and T7.1 have an activity of over 80 %.

Example B6: Activity against Myzus persicae (systemic application)

Pea seedlings are infected with *Myzus persicae*, and their roots are subsequently placed into a spray mixture comprising 400 ppm of active ingredient. The seedlings are then incubated at 20°. 3 and 6 days later, the percentage reduction in the population (% activity) is determined by comparing the number of dead aphids between the treated and untreated plants.

In this test, compounds listed in the Tables 1 to 71 show good activity.

Example B7: Activity against Plutella xylostella

Young cabbage plants are sprayed with an aqueous emulsion spray mixture comprising 400 ppm of active ingredient and, after the spray coating has dried on, populated with 10 caterpillars (3rd instar) of *Plutella xylostella* and introduced into a plastic container. 3 days later, the percentage reduction in the population and in the feeding damage (% activity) are determined by comparing the number of dead caterpillars and the feeding damage between the treated and untreated plants.

In this test, compounds listed in the Tables 1 to 71 show good activity. In particular, the compounds T1.1, T1.3, T7.1 and T7.3 have an activity of over 80 %.

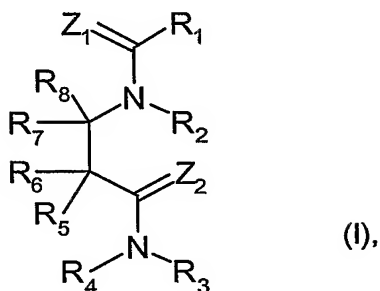
Example B8: Activity against Spodoptera littoralis

Young soya plants are sprayed with an aqueous emulsion spray mixture comprising 400 ppm of active ingredient and, after the spray coating has dried on, populated with 10 caterpillars (1st instar) of *Spodoptera littoralis* and introduced into a plastic container. 3 days later, the percentage reduction in the population and in the feeding damage (% activity) are determined by comparing the number of dead caterpillars and the feeding damage between the treated and untreated plants.

In this test, compounds listed in the Tables 1 to 71 show good activity. In particular, the compounds T1.1, T1.3, T7.1 and T7.3 have an activity of over 80 %.

What is claimed is:

1. A compound of the formula



in which

Z_1 is an oxygen atom; or a sulfur atom;

Z_2 is an oxygen atom; or a sulfur atom;

R_1 is an aryl or heteroaryl group, which is unsubstituted or substituted;

R_2 is hydrogen; or an organic substituent;

R_3 is hydrogen; or an organic substituent;

R_4 is hydrogen; or an organic substituent;

or R_3 and R_4 , taken together, form, together with the nitrogen atom, to which they are attached, a ring, which is unsubstituted or substituted;

R_5 is hydrogen; or an unsubstituted or substituted alkyl group; or forms, taken together with R_8 or with a monovalent substituent attached to that atom of R_6 , via which atom R_6 is directly connected with the carbon atom, shown in the formula I, which carries R_5 , one additional bond;

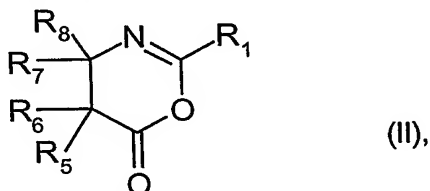
R_6 and R_7 , taken together, form, together with the two carbon atoms, shown in the formula I, to which atoms they are attached, a bicyclic ring system, which ring system is carbocyclic or heterocyclic, which ring system is substituted, in the manner shown in the formula I, by the four substituents $-N(R_2)-C(=Z_1)-R_1$, $-C(=Z_2)-N(R_3)-R_4$, R_5 and R_8 , and which ring system is optionally further substituted;

and R_8 is hydrogen; or an unsubstituted or substituted alkyl group; or forms, taken together with R_5 or with a monovalent substituent attached to that atom of R_7 , via which atom R_7 is directly connected with the carbon atom, shown in the formula I, which carries R_8 , one additional bond,

or, where appropriate, a tautomer thereof, in each case in free form or in salt form.

2. A compound according to claim 1 of the formula I, in which Z_1 is an oxygen atom, or, where appropriate, a tautomer thereof.
3. A compound according to claim 1 of the formula I, in which Z_2 is an oxygen atom, or, where appropriate, a tautomer thereof.
4. A compound according to claim 1 of the formula I, in which R_1 is a phenyl, pyridyl or pyrazolyl group, which is unsubstituted or preferably substituted, or, where appropriate, a tautomer thereof.
5. A compound according to claim 4 of the formula I, in which R_1 is a pyrazol-5-yl group, which is substituted in the 3-position by halogen, halo- C_1 - C_6 alkyl or halo- C_1 - C_6 alkoxy and in the 1-position by a pyrid-2-yl group, which group is substituted in the 3-position by chlorine or bromine, or, where appropriate, a tautomer thereof.
6. A compound according to claim 1 of the formula I, in which R_2 is hydrogen or C_1 - C_6 alkyl, or, where appropriate, a tautomer thereof.
7. A compound according to claim 1 of the formula I, in which R_3 is hydrogen or C_1 - C_6 alkyl, or, where appropriate, a tautomer thereof.
8. A compound according to claim 1 of the formula I, in which R_4 is C_1 - C_6 alkyl, or, where appropriate, a tautomer thereof.
9. A compound according to claim 1 of the formula I, in which R_5 and R_8 , taken together, are a bond, or, where appropriate, a tautomer thereof.
10. A compound according to claim 1 of the formula I, in which the two carbon atoms, shown in the formula I, to which atoms R_6 and R_7 are attached, are two ring members of an aromatic ring, or, where appropriate, a tautomer thereof.
11. A process for the preparation of a compound according to claim 1 of the formula I or, where appropriate, a tautomer thereof, in each case in free form or in salt form, which comprises

a) to prepare a compound of the formula I, in which Z_1 is an oxygen atom; Z_2 is an oxygen atom; and R_2 is hydrogen, or, where appropriate, a tautomer and/or salt thereof, reacting a compound of the formula



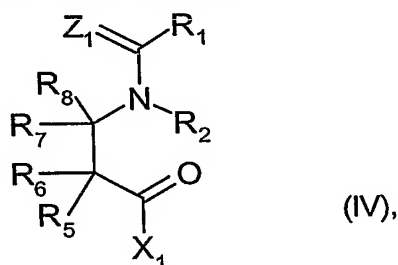
in which R_1 , R_5 , R_6 , R_7 and R_8 have the meanings given for the formula I, or, where appropriate, a tautomer and/or salt thereof with a compound of the formula



in which R_3 and R_4 have the meanings given for the formula I, or, where appropriate, with a tautomer and/or salt thereof or,

b) to prepare a compound of the formula I, in which Z_1 is a sulfur atom; and Z_2 is a sulfur atom, or, where appropriate, a tautomer and/or salt thereof, reacting a compound of the formula I, in which Z_1 is an oxygen atom; and Z_2 is an oxygen atom, or, where appropriate, a tautomer and/or salt thereof with a sulfurising agent or,

c) to prepare a compound of the formula I, in which Z_2 is an oxygen atom, or, where appropriate, a tautomer and/or salt thereof, reacting a compound of the formula

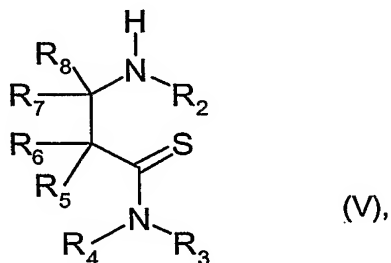


in which Z_1 , R_1 , R_2 , R_5 , R_6 , R_7 and R_8 have the meanings given for the formula I; and X_1 is a leaving group, or, where appropriate, a tautomer and/or salt thereof with a compound of the formula

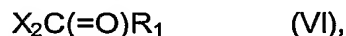


in which R_3 and R_4 have the meanings given for the formula I, or, where appropriate, with a tautomer and/or salt thereof or,

d) to prepare a compound of the formula I, in which Z_1 is an oxygen atom; and Z_2 is a sulfur atom, or, where appropriate, a tautomer and/or salt thereof, reacting a compound of the formula



in which R_2 , R_3 , R_4 , R_5 , R_6 , R_7 and R_8 have the meanings given for the formula I, or, where appropriate, a tautomer and/or salt thereof with a compound of the formula



in which R_1 has the meaning given for the formula I; and X_2 is a leaving group, or, where appropriate, with a tautomer and/or salt thereof

and/or converting a compound of the formula I or, where appropriate, a tautomer thereof, in each case in free form or in salt form, into another compound of the formula I or, where appropriate, a tautomer thereof, separating an isomer mixture, which can be obtained in accordance with the process, and isolating the desired isomer and/or converting a free compound of the formula I or, where appropriate, a tautomer thereof into a salt or a salt of a compound of the formula I or, where appropriate, a tautomer thereof into the free compound of the formula I or, where appropriate, a tautomer thereof or into another salt.

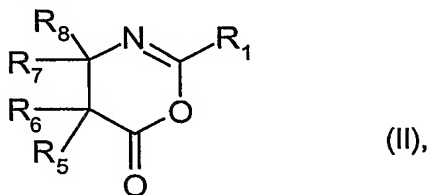
12. A pesticidal composition, which comprises at least one compound according to claim 1 of the formula I or, where appropriate, a tautomer thereof, in each case in free form or in agrochemically utilizable salt form, as active ingredient and at least one auxiliary.

13. A composition according to claim 12 for controlling insects or representatives of the order Acarina.

14. A process for the preparation of a composition according to claim 12, which comprises intimately mixing and/or grinding the active ingredient with the auxiliary (auxiliaries).

15. The use of a compound according to claim 1 of the formula I or, where appropriate, a tautomer thereof, in each case in free form or in agrochemically utilizable salt form, for the preparation of a composition according to claim 12.
16. The use of a composition according to claim 12 for controlling pests.
17. The use according to claim 16 for controlling insects or representatives of the order Acarina.
18. The use according to claim 16 for the protection of plant propagation material from the attack by pests.
19. A method for controlling pests, which comprises applying a composition according to claim 12 to the pests or their environment.
20. A method according to claim 19 for controlling insects or representatives of the order Acarina.
21. A method according to claim 19 for the protection of plant propagation material from the attack by pests, which comprises treating the propagation material or the site, where the propagation material is planted.
24. Plant propagation material treated in accordance with the method described in claim 21.

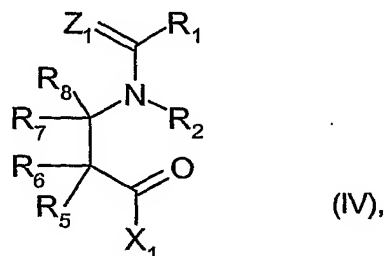
25. A compound of the formula



in which R_1 , R_5 , R_6 , R_7 and R_8 have the meanings given in claim 1 for the formula I, or, where appropriate, a tautomer thereof, in each case in free form or in salt form.

26. The use of a compound according to claim 25 of the formula II or, where appropriate, a tautomer thereof, in each case in free form or in salt form, for the preparation of a compound according to claim 1 of the formula I or, where appropriate, a tautomer thereof.

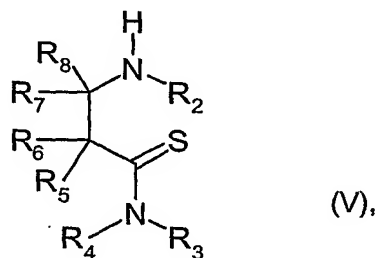
27. A compound of the formula



in which Z_1 , R_1 , R_2 , R_5 , R_6 , R_7 and R_8 have the meanings given in claim 1 for the formula I; and X_1 is a leaving group, or, where appropriate, a tautomer thereof, in each case in free form or in salt form.

28. The use of a compound according to claim 27 of the formula IV or, where appropriate, a tautomer thereof, in each case in free form or in salt form, for the preparation of a compound according to claim 1 of the formula I or, where appropriate, a tautomer thereof.

29. A compound of the formula

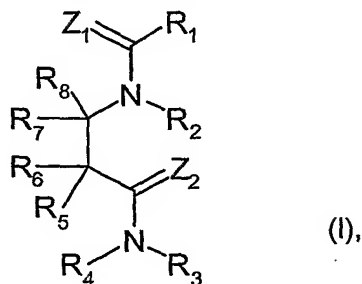


in which R_2 , R_3 , R_4 , R_5 , R_6 , R_7 and R_8 have the meanings given in claim 1 for the formula I, or, where appropriate, a tautomer thereof, in each case in free form or in salt form.

30. The use of a compound according to claim 29 of the formula V or, where appropriate, a tautomer thereof, in each case in free form or in salt form, for the preparation of a compound according to claim 1 of the formula I or, where appropriate, a tautomer thereof.

Abstract

Compounds of the formula



in which

Z_1 is an oxygen atom; or a sulfur atom;

Z_2 is an oxygen atom; or a sulfur atom;

R_1 is an aryl or heteroaryl group, which is unsubstituted or substituted;

R_2 is hydrogen; or an organic substituent;

R_3 is hydrogen; or an organic substituent;

R_4 is hydrogen; or an organic substituent;

or R_3 and R_4 , taken together, form, together with the nitrogen atom, to which they are attached, a ring, which is unsubstituted or substituted;

R_5 is hydrogen; or an unsubstituted or substituted alkyl group; or forms, taken together with R_8 or with a monovalent substituent attached to that atom of R_6 , via which atom R_6 is directly connected with the carbon atom, shown in the formula I, which carries R_5 , one additional bond;

R_6 and R_7 , taken together, form, together with the two carbon atoms, shown in the formula I, to which atoms they are attached, a bicyclic ring system, which ring system is carbocyclic or heterocyclic, which ring system is substituted, in the manner shown in the formula I, by the four substituents $-N(R_2)-C(=Z_1)-R_1$, $-C(=Z_2)-N(R_3)-R_4$, R_5 and R_8 , and which ring system is optionally further substituted;

and R_8 is hydrogen; or an unsubstituted or substituted alkyl group; or forms, taken together with R_5 or with a monovalent substituent attached to that atom of R_7 , via which atom R_7 is directly connected with the carbon atom, shown in the formula I, which carries R_8 , one additional bond,

and, where appropriate, tautomers thereof, in each case in free form or in salt form, can be used as agrochemical active ingredients and can be prepared in a manner known per se.